VOL. XXXII. AUGUST, 1904. NO. 2.

AMERICAN

CHEMICAL JOURNAL

A NEW ELECTRIC FURNACE AND VARIOUS OTHER ELECTRIC HEATING APPLIANCES FOR LABORATORY USE.[1]

BY H. N. MORSE AND J. C. W. FRAZER.

Having found in the electrolytic process[2] a ready and satisfactory means of depositing semi-permeable membranes, and having overcome, to some extent, the mechanical difficulties which are encountered in assembling, in a secure manner, the various parts of the osmotic cell, we turned our attention to the third, and probably the most difficult, problem which must be solved before any attempt to devise a practicable method for the direct measurement of osmotic pressure can succeed—namely, to the porous wall on which the semi-permeable membrane is deposited.

Thin sections of the walls of the cells in which the high pressures recorded elsewhere[3] had been developed, as well as

[1] The work of the authors, undertaken with the purpose of perfecting, if possible, a practicable method for the measurement of osmotic pressure, has been carried on with the aid of grants from the Carnegie Institution. The present article describes some of the incidental results of that work.

[2] This JOURNAL, **26**, 80; **28**, 1; **29**, 173.

[3] *Ibid.*, **28**, 1.

of cells which had conducted themselves unsatisfactorily, were studied under the microscope, and it was found that there are certain well-marked characteristic differences of porous wall structure between those cells which conduct themselves well and those in which it is impossible to develop any considerable pressure.

These differences will be described more fully in a later article in connection with an account of our attempts to produce in the laboratory a porous clay wall suitable for the construction of osmotic cells. It is sufficient, for present purposes, to state that we soon found, in the course of our study of thin sections, that probably one reason for the more or less complete failure of more than nine-tenths of the porous vessels made at the potteries is the too rapid expulsion of the chemically combined water during the baking of the clay, which results in the production, by the escaping steam, of relatively large channels through the wall material. The openings of these channels on the interior surface of the vessels are spanned—not filled—by the membrane, and when the membrane is subjected to pressure it is ruptured at the unsupported points.

It appeared that some method of baking must be devised which would make practicable a very precise regulation through the range of temperatures within which clay loses the greater portion of its water. The electric furnace in which the resistance of platinum wire is utilized to secure high temperatures appeared likely to answer our purpose, and we procured one of a type which has had some currency in this country. In it the wires are threaded through holes in the interior of the sides and bottom of the furnace so that the heat generated in the wires must penetrate a considerable thickness of clay before reaching the space to be heated. With such an arrangement it requires a very long time to obtain, with any given current, the temperature which that current will eventually maintain in the furnace. In the case of the instrument here mentioned, from seven to nine hours were required to reach a constant temperature with a constant current, and

close regulation was therefore impossible. Another objection to this furnace was its wastefulness. At 1250° the consumption of electrical energy was equivalent to 1200 watts. A little above this temperature the sheet-iron casing burned out and was replaced by one of baked fire-clay, provision being made for an air space between it and the furnace proper. The furnace behaved somewhat better thereafter, both in respect to the time required to reach a constant temperature and the amount of current necessary to maintain it. But the improvement was not sufficient to justify its employment for our purposes and it was discarded.

The defects of the abandoned furnace were due to the faulty principles on which it was constructed—to the burial of the wires within the walls of the space to be heated, and to the absence of vacant enclosed spaces between it and the outer air. In the furnace about to be described these faults are avoided. The furnace represented by the accompanying figures is not that which is employed by us as a kiln for the burning of clay vessels, but is one which was designed for the fusion of materials, *e. g.*, silicates, in crucibles. It, however, does not differ from the kiln except in respect to dimensions and the fact that in the kiln—owing to its larger size—two wires in parallel are employed, while in the smaller instrument a single wire suffices, or, if two are present, they are generally used in series.

The furnace proper is represented by Fig. I. The three hard-burned perforated clay rings, *a*, *b*, and *c*, are held in place by three platinum rods made from No. 16 wire (B & S gauge). The ends of these rods are threaded, and each end is provided with two small platinum nuts, between which the rings *a* and *c* are firmly fastened. The purpose of the ring *b* is to keep the crucible from coming in contact with the platinum wires. It is adjustable up or down, but may be fixed in any desired position by twisting short pieces of wire about the rods. The internal diameters of *b* and *c* are equal, while that of *a* is smaller in order to furnish a rest for the crucible support. Each ring is provided with 60 perforations, in two rows of 30 each, through which the wire (No. 26 B & S gauge) is

woven up and down in the manner shown in the figure. The inner row of wires also crosses from side to side under *a*. The

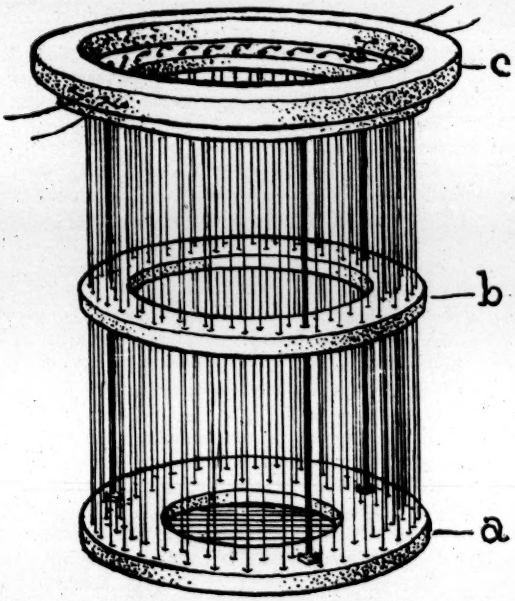


Fig. I.

total height of the furnace as represented in Fig. I. is 80 mm. and the total length of the wire is 16 feet. The platinum rods serve two important purposes. They support the whole weight of the furnace and its contents and thus prevent any stretching of the wires while hot, and, having at all times about the same temperature as the wires, they keep them per-

fectly straight and thus prevent any danger of short circuits through contact of adjacent strands.

The furnace as represented in Fig. I. is surrounded by the

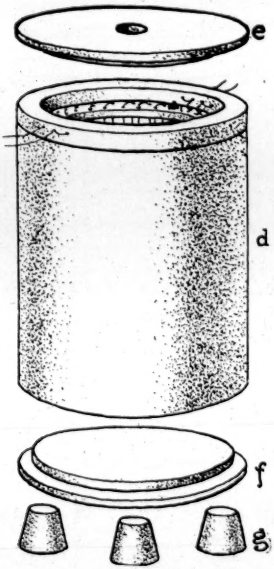


Fig. II.

clay cylinder *d*, as shown in Fig. II., the ring *c*, Fig. I., resting upon the upper edge of *d*. The cylinder *d* is provided with the perforated cover *e* and the bottom *f*, which rests upon the three truncated clay cones, *g*. The perforation in *e* serves for the introduction of a thermometer or pyrometer.

Fig. III. represents a cylinder, *h*, of larger dimensions,

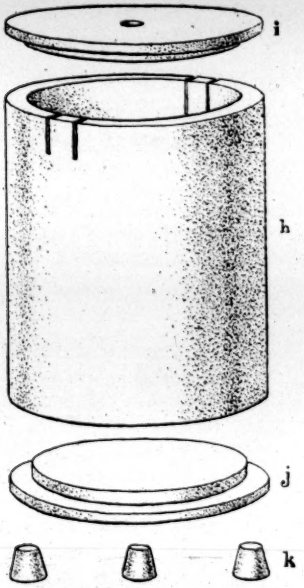


Fig. III.

which surrounds *d*. It is also furnished with a perforated cover, *i*, a bottom, *j*, and the supports *k*.

The complete furnace is shown in Fig. IV., in which *l* is a Le Chatelier pyrometer, *m* a galvanized iron cylinder with cover—both of which are lined and covered with asbestos paper, *n* a series of asbestos boards with ventilating spaces between them, *o* a block of soapstone, and *p* a board on which the whole arrangement rests and can be moved without disturbing any of the parts. *q* and *r* are firmly fixed steel rods which serve to connect the wires coming from the furnace with the external circuit and to protect the former from in-

jury through strains of any kind. *s,s* are short pieces of pipe stem which keep the platinum wires from contact with the metallic cylinder *m*. The crucible support *t* is made as light and open as possible, coming in contact with the crucible at three points only.

The material which was used in making the clay parts of the furnace was a mixture of equal portions by weight of a fire-clay from Mt. Savage, Md., and a clay from Edgar, Fla. Neither of these materials, taken alone, was suitable for the purpose. The fire-clay was lacking in adhesive qualities and crumbled easily after baking, unless heated to a very high temperature, while articles made of the clay from Florida exhibited a tendency to crack, both during the air-drying and the baking periods. The mixture of the two was easily formed and the moulded pieces were quite free from a tendency to crack, either while drying in the air or during the burning process. The burned products were very tough and remained porous at high temperatures, and therefore showed little tendency to stick to the platinum wires. The clay from Florida had already been washed in the manner usual in preparing such material for the potteries. The coarser matter in the fire-clay was removed by sifting, and the two clays were thoroughly mixed by passing them repeatedly through a fine sieve. The smaller articles—the rings and the inner cylinders with their covers—were burned in the laboratory in a Seger experimental furnace, while the larger outer cylinders were burned for us at the pottery of D. F. Haynes & Son, to whom we are indebted for many other courtesies during the course of our work.

Since any one who wishes to reproduce this furnace or to provide himself with a similar one will probably have to act as his own potter, it may be of service to enter somewhat into mechanical details. The making of the perforated rings, *a*, *b*, and *c*, is the most troublesome part of the task though it presents no very great difficulties.

In the hard wood block *a*, Fig. V., a cavity is turned on the lathe which has the form and dimensions of the ring *c* when

first molded—allowance having been made, of course, for the shrinkage of the clay in burning. The holes for the two rows of wires and the three posts are then bored and into each

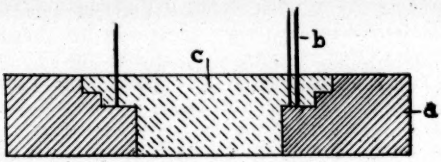


Fig. V.

hole is inserted a closely fitting steel rod *b*—pieces of small knitting needles being used for the purpose. The cavity is filled with plaster of Paris, giving the piece *c* upon which in turn, with the rods in place, the plaster cast *a*, Fig. VI., is

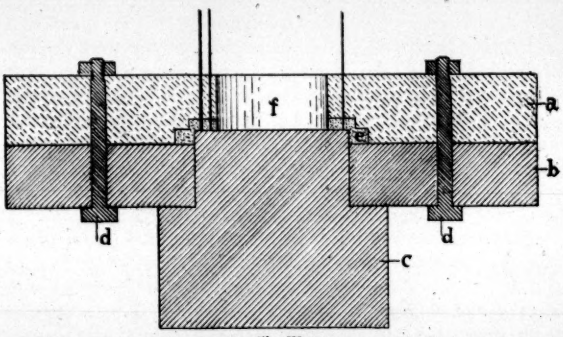


Fig. VI.

made. The pieces *b* and *c*, Fig. VI., are of hard wood and are turned to correct form and dimensions on the lathe. The parts *a* and *b* are fastened together by the bolts *d*,*d*. When the ring *e* is to be made, the clay is moulded into its place in *a*, *b* is bolted to *a*, and *c* is crowded into position. The perforations in the ring are then made by pushing the needles through the holes in *a*. Finally, the excess of the clay,

which, by the procedure described, has all been crowded into the cavity *f*, is trimmed away, leaving the inside of the ring round and smooth. The description here given relates to the upper ring *c*, Fig. I. The middle and bottom rings are made in a similar manner and the process need not, therefore, be explained.

Fig. VII. represents the form of mold in which the cylin-

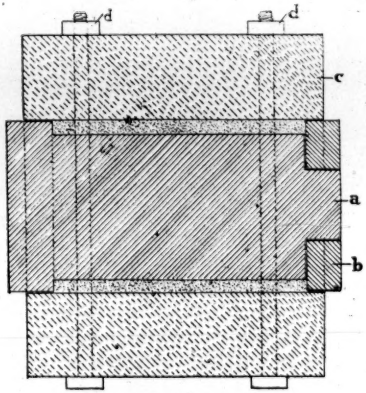


Fig. VII.

ders *d* and *h*, Figs. II. and III., are made. *a* is a circular hard wood core whose external diameter is equal to the internal diameter of the clay cylinder, except at the ends, where it is equal to the external diameter of the cylinder. *b* is a ring which may be removed. The core *a* is tapered slightly toward the end having the ring in order to facilitate its withdrawal after molding the clay. *c* and *c* are the two halves of a plaster of Paris mold which are held together by the bolts *d*,*d*. The wet clay is rolled out flat and to the right thickness, cut to shape, and wrapped about the wooden core which has previously

been covered with oil to prevent sticking. In order to perfect the outside of the cylinder, the core with the clay on it is rolled along the table top and then placed in the plaster mold. As soon as the clay becomes sufficiently stiff, the core is withdrawn.

Fig. VIII. represents the arrangement for making the tops

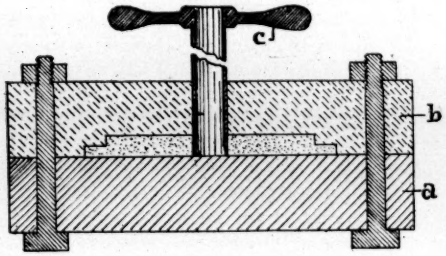


Fig. VIII.

and the bottoms of the cylinders. *a* is a hard wood block, *b* is a block of plaster of Paris which has been cast about a model of a top or bottom, and *c* is a cork borer which is used to cut a hole when a top is to be made.

The wiring of the furnace is accomplished in the following manner: The wire is straightened out and fastened at the two ends. A current is then sent through it until it glows throughout its entire length. Or, with the wire in one hand and a lamp in the other, it is heated to redness, section by section, from end to end. Either process will remove a tendency on the part of the wire to wind up or twist, but the first is the better method because a wire which has been treated in the second way will exhibit irregular resistance, owing to unequal stretching of the different parts while hot. After threading the wire through the three holes belonging to each vertical strand, the strand is heated to redness with the flame

of the lamp or, better, by means of an electric current, and while the wire is hot and under a slight strain it is fastened in place by inserting a steel pin in the last hole, which must not be removed until after the succeeding strand has been finished in the same manner. If a little pains is taken in these matters, every strand will be perfectly straight and the furnace, when finished, will present a neat and satisfactory appearance.

The first step to be taken with the completed furnace is to calibrate it, that is, to determine its resistance for every temperature up to the limit to which it is afterwards to be heated, for it will then be feasible at all times, without the aid of a pyrometer, to maintain in it with certainty any desired temperature or to ascertain at any time what the temperature in it is. The furnace, in fact, becomes by virtue of such a calibration a resistance pyrometer.

For the calibration of the kilns used in the baking of cells and of the laboratory furnace just described we had at our disposal mercury thermometers registering to 550°, a Le Chatelier platinum platinum-rhodium pyrometer, and a Keiser-Schmidt decimillivoltmeter, all of which had been tested at the German Physikalisch-Technische Reichsanstalt. We give below in tabular form the data for the crucible furnace up to 967°. The calibration was not carried higher because the temperature 950° is sufficient for any ordinary crucible work. The temperatures given are probably correct to within 5° or less. The voltmeter which was used to measure the electromotive force developed at the junction of the platinum and platinum-rhodium wires is furnished with two scales, one in which each division has the value of a decimillivolt, and another in which a division corresponds to 20° of temperature. Unfortunately the needle of this instrument is unnecessarily thick and clumsy near the free end, making possible some errors of parallax in reading. These, however, could not amount to more than one-fourth of a division on either scale. The ammeters and voltmeters used in measuring the current were of the best Weston types.

Current.	Voltage.	Resistance.	Watts.	Temperature.
2.5	33.7	13.48	84.25	383°
2.6	36.0	13.846	93.60	407°
2.7	38.5	14.259	106.38	434°
2.8	41.0	14.671	114.80	463°
2.9	43.6	15.034	126.44	488°
3.0	47.4	15.80	142.20	526°
3.1	50.2	16.193	155.62	558°
3.2	52.7	16.468	168.72	587°
3.3	55.3	16.757	182.49	615°
3.4	58.3	17.147	198.22	640°
3.5	61.2	17.486	214.20	663°
3.6	64.3	17.861	231.48	690°
3.7	66.9	18.081	247.53	710°
3.8	70.1	18.447	266.38	741°
3.9	73.3	18.795	285.87	766°
4.0	76.3	19.075	305.20	793°
4.1	79.5	19.390	325.55	813°
4.2	82.5	19.643	338.25	840°
4.3	85.3	19.837	366.79	867°
4.4	88.7	20.159	390.28	888°
4.5	92.0	20.444	414.00	914°
4.6	95.0	20.652	437.00	940°
4.7	98.0	20.851	460.60	967°

It will be readily understood that an accurately calibrated resistance furnace is theoretically an admirable instrument for the study of reactions at high temperatures, for, if external conditions are constant, it will always require the same amount of electrical energy to maintain any given temperature in the empty furnace, or, what is the same thing, a given amount of electrical energy is bound to maintain in it always a certain fixed temperature. If now any reaction involving the disappearance or evolution of heat takes place within the heated space, the amount of electrical energy required to maintain the temperature at which it takes place will be increased or diminished, according as the reaction is endothermic or exothermic, and the difference, if it can be ascertained, will serve as a measure of the heat energy of the reaction.

There is little difficulty in discovering at what temperatures reactions involving any considerable heat effects take place in an electric furnace. In baking our cells, for example,

while the water is being expelled from the clay the amount of current required to maintain a given temperature is very noticeably larger than that required to maintain the same temperature in the empty kiln, showing that a reaction involving the loss of heat is going on within. Again, when a fusible substance is heated in the furnace and the temperature of fusion is reached, there is noticed an increase in the flow of the current without any corresponding increase in the resistance of the platinum wire, *i. e.*, in the temperature of the furnace. The increased flow of current continues for a time and then diminishes to its original volume, showing that the fusion is finished. If the furnace has been calibrated, a determination of its resistance during the time of the increased flow of current will give the melting-point of the substance. In this way we found the fusing-point of sodium carbonate to be between 860° and 863°. The exact time of fusion may also be ascertained by arranging to have the sinking of a platinum weight into the softened material either close or break a circuit in which there is a sensitive ammeter.

In order that the results of the study of reactions by means of the electric furnace may have a high degree of precision, certain difficulties must be overcome. The principal one of these is the length of time required to establish equilibrium between the temperature within the furnace and that of the external air. During the calibration of the furnace under consideration, we raised the current each time by 0.1 ampere, which gave an average rise of temperature of about 26°.4 for each increase of current, the minimum being 20° and the maximum 38°. Usually about one-half of the rise occurred within the first five minutes, while the remainder occupied from fifty to sixty minutes with a gradually decreasing rate, which finally became very slow.

The tardiness of this adjustment between internal and external temperature conditions—despite the favorable location of the wires with respect to the space heated and the double enclosed air spaces surrounding it—lessens the precision of the results when the furnace is employed to determine fusing-points and to ascertain the temperatures at which reactions

(loss of water, etc.) occur, and a remedy is called for. The most promising remedy which suggested itself was to cover the exterior of the furnace, where it is in contact with the outer air, with some substance which conducts electricity, but whose conductivity increases with rise in temperature, and to divide the circuit so that while the major portion of the current passes through the furnace, another portion passes over and heats the surface in contact with the air. The effect of such an arrangement would be to compensate automatically for the increased loss of heat to the outer air which attends any rise in the temperature of the furnace, for as the temperature rises, the conductivity of the circuit through the furnace would diminish, while that of the outer circuit would increase and a larger proportion of the total current would therefore take the latter course.

Since graphite is a substance which not only conducts electricity, but one whose conductivity increases with rise in temperature, it seemed likely to be of service in our scheme, and we began to test the suitability for heating purposes of surfaces covered with that material. One result of this work has been the construction of a number of air-baths for general use in the laboratory, some of which we will here describe.

Soapstone is undoubtedly the best of all available materials on which to spread the graphite for heating purposes. It is easily cut to any desired form, its surface can be made very smooth, which is essential to the best results, and, above all, it withstands better than any other non-conducting material great and sudden changes of temperature.

We take pleasure in acknowledging here our indebtedness to the Alberene Stone Company, which provided us, free of expense to ourselves, with an abundance of this material, and also to the Joseph Dixon Crucible Company, which presented us with liberal quantities of different varieties of specially prepared graphite.

Figs. IX. and X. represent two forms of graphite stoves for ordinary hot-air baths. *a*, Fig. IX., is a soapstone block of convenient size for the usual rectangular copper hot-air bath.

It is seen in place in Fig. XI. *b*,*b*,*b*,*b* are strips of iron which are bolted to the block at the ends, the central bolt at each end serving for the attachment of the wires of the circuit.

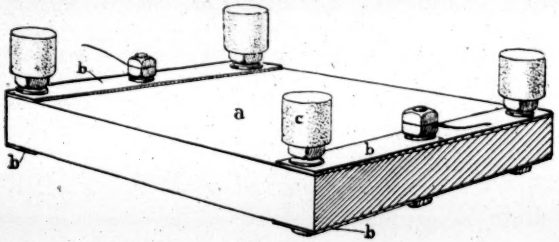


Fig. IX.

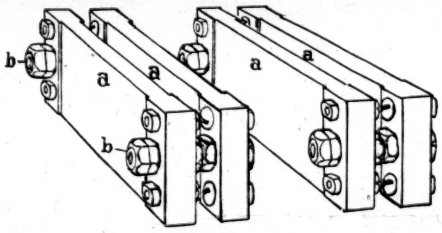


Fig. X.

The corner bolts, which are longer than the others, are covered by the soapstone pieces *c*,*c*,*c*,*c*. On these rests the perforated metallic shelf, as seen in Fig. XI.

Fig. X. represents another arrangement for heating the same bath, which has the advantage that the surfaces on which the heat is generated are vertical. *a*,*a*,*a*,*a* are narrow strips of soapstone of such dimensions that when bolted together by twos, as shown in the figure, three pairs of them can rest on the bottom of the bath, leaving room between the

ends for the insertion of mica plates to prevent electrical contact. Each end of every soapstone strip is provided with two iron plates which are bolted to the stone in the manner shown. Two strips, thus furnished, are fastened together by the longer bolts *b*,*b*, which are also utilized for the attachment of wires.

Fig. XI. represents the arrangement as a whole. *b* is a

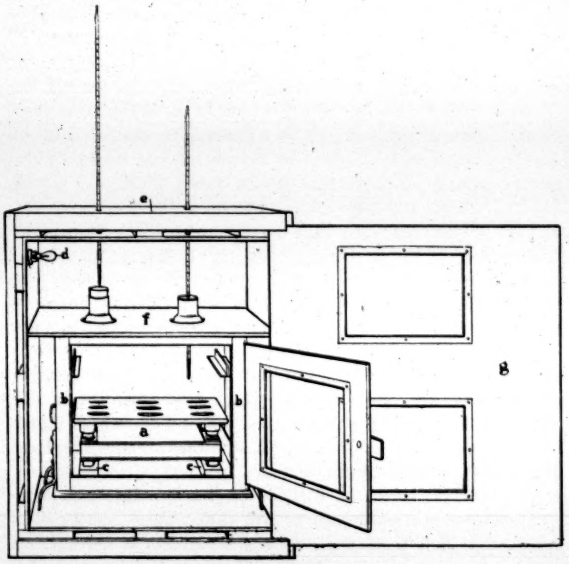


Fig. XI.

copper-bath of the usual form, having a mica window in its door. The stove *a*, which may be of either of the forms represented in Figs. IX. and X., rests on the soapstone strips *c*,*c*. The inner vertical walls of the copper bath may be lined to advantage with thin asbestos board, but in that case it is

well to cover the exposed surface of the board with aluminium paint, which will prevent the lodgment of dust and the shedding of particles of asbestos. The wires of the stove pass horizontally through the sides of the copper bath and the outer compartment to the exterior of the wooden box which encloses the whole, where each wire terminates in a binding post screwed into the box. Where the wires pass through the copper walls they are prevented from coming in contact with the metal by short pieces of clay pipe stem. When a stove such as is shown in Fig. X. is used, each of the three pairs of plates is provided with independent wires and binding posts, any required combinations of the individual pairs in parallel or series being made more conveniently on the outside than on the inside of the bath. *d* is a diminutive electric lamp of small voltage, which serves to illuminate the scales of the thermometers. The current for it comes through a shunt from the stove, and a switch is fastened to the outside of the box for the purpose of closing and breaking the lamp circuit. The voltage of the lamp must be suited, of course, to the fall in potential of the stove. The interior of the wooden box is lined on all sides, except the front, with asbestos board in such a manner as to leave confined air spaces between the asbestos and the wood. The surface of the lining boards is also covered with aluminium paint. *f* is a closely fitting shelf of asbestos board (also painted), which rests upon the copper bath and is supported at the ends. *g* is a door which slides in grooves in the wooden box. It contains two mica windows and is made from asbestos board.

The shelf *f* divides the interior of the box into two compartments whose temperatures will differ quite widely from each other and from the temperature which is maintained within the copper bath. This difference can, however, be diminished, if desired, by replacing *f* by a more or less open shelf which permits circulation of air between the upper and lower spaces. Each of the heated compartments, including the copper bath, should be provided with two properly located ventilating tubes running to the outside of the wooden box. Porcelain insulating tubes are well adapted for this pur-

pose. They may be closed with corks, to prevent loss of heat, when not needed.

Fig. XII. is a cross-section of a furnace used by the authors

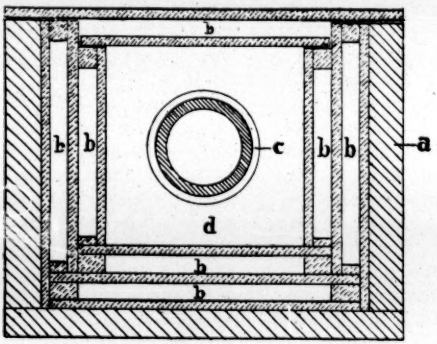


Fig. XII.

for heating substances enclosed in tubes (Carius tubes, etc.). *a* is a wooden box 625 mm. in length, which is so lined and covered with asbestos board as to give the closed air spaces designated by *b*. *c* is a porcelain tube having the length of the box and an internal diameter of 30 mm. The space *d* about *c* is sufficient to accommodate larger tubes when required to do so. An iron tube of thin wall is slipped into *c* to aid in distributing the heat and to prevent injury to the porcelain tube when explosions occur. Fig. XIII. shows an iron collar which is fastened to each end of the porcelain tube and serves for the attachment of the wires.

Fig. XIII.

The rubbing of ground, dry graphite upon the smooth surface of soapstone or porcelain does not give a sufficiently heavy coating of the material to conduct the requisite amount of current. A thicker covering of graphite can be obtained by repeated applications of it, in a wet condition, with a flat camel's hair brush. The surface to which it is applied must, however, be hot enough to evap-

orate the water almost instantaneously, otherwise the deposit will be quite uneven. The results obtained by the last method are nevertheless unsatisfactory. The material lacks adhesiveness and when an attempt is made to harden it by polishing with a stiff brush, much of the graphite is detached and the surface which is produced is easily injured by handling or by contact with other objects.

Better results are secured by mixing the ground graphite with washed and bolted clay and making a paste of the mixture with water. But the best results have been obtained with the paste form of a well-known stove polish,[1] and we shall describe somewhat in detail our method of applying it since a correct procedure in this matter is of much importance. The iron plates at the ends of the soapstone block (Fig. IX.) or of the strips (Fig. X.) are removed, and their inner surfaces, and also those portions of soapstone which are covered by the plates, are evenly spread with a rather thick layer of the paste. The plates are then replaced and bolted together. The block or strip (connected in the circuit in which there is also an ammeter) is placed on a piece of asbestos board or of some other non-conducting material, which is heated by a lamp. When the stone is hot enough to evaporate water with rapidity, but without "sputtering," the paste, much thinned with water, is evenly applied with a flat camel's hair brush whose width is about 25 mm. The whole stone should be covered each time, but the brush should not pass more than once over any one spot. After each application, the surface is vigorously polished with a stiff tooth-brush.

An even distribution of the graphite is of great importance, for, if it is unevenly distributed, the resistance in different regions will vary and more heat will be developed at some points than others. The result, in the case of a carelessly prepared stove, is that the graphite burns out in certain spots while the whole amount of heat developed is much less than the surface ought to bear with safety.

As soon as the conductivity of the graphite covering has increased to a point where the current suffices to maintain the

[1] The "Rising Sun."

proper temperature of the stove, it is removed from the asbestos board and the surface is carefully explored with the voltmeter with reference to the uniformity of the distribution of resistance. The subsequent applications of the graphite are regulated with a view to securing uniform conductivity over the whole surface, that is, those spots which are found by the voltmeter to exhibit a higher resistance are painted more thickly than the others. With care and a little experience, it becomes easy to prepare in a short time a stove on which the graphite is very evenly distributed and so firmly adherent that it will not visibly soil the fingers in handling. As the painting proceeds, the surface is apt to become so hot that the water is evaporated with explosive violence, and the surface presents a spotted appearance, owing to an uneven spreading of the material. When this occurs, the circuit must be broken and the stone allowed to cool before making an application.

The thickness of the graphite covering should be regulated with a view to the most economical expenditure of energy in the subsequent use of the stove, in other words, with a view to dispensing with as much as possible of the external resistance which is always inserted in the circuit for the purpose of regulating the temperature of the bath. In this connection, the advantage of the stove represented in Fig. X. will be seen. It consists, as has already been stated, of three sections of two plates each, each section having its two wires running to the outside of the wooden box, where they terminate in binding posts. With such an arrangement, it is easy, as a rule, to make a combination of the sections which will suit the voltage of the current which is to be used and therefore to reduce to a minimum the amount of external resistance required for the regulation of the bath. In preparing the stove of this kind which we have in use, the application of the graphite to each strip was continued until, with a fall of potential of 50 volts, it conducted one ampere of current. The temperature of the stone at the time of finishing the strips was not always the same, so that the resistance at any given

temperature varies somewhat from strip to strip, but not sufficiently to lead to difficulties.

It is important for users of graphite baths to know approximately what temperature a graphite surface will bear without injury. It is unfortunate that an admixture of clay is necessary in order to improve its spreading and adhesive qualities, for the clay begins to lose its water at about 425°, and at this point a change in the resistance of the material occurs. Speaking generally, it may be stated that the temperature of the stove itself should not be allowed to rise above 400°. How nearly the temperature of a bath may be made to approach this limit will depend, of course, upon the volume of the space to be heated as compared with the area of the heating surface. In small baths we have succeeded in keeping a constant temperature of 400°, but there is danger that, in attempting to reach so high a temperature too quickly, the clay will become overheated and lose some of its water. We have found it safe and practicable with properly prepared stoves having a suitable area of heating surface to maintain in a considerable variety of baths any temperature up to 350°. A somewhat higher temperature may be maintained, but always at some risk to the stove. The principal danger lies in using too large a current while raising the temperature of the bath.

We give below the data relating to some of the baths which we have in use in order that a judgment may be formed respecting the economical advantage of using electricity rather than gas for ordinary laboratory purposes.

Bath No. 1 was like that shown in Fig. XI. The stove was of the kind represented in Fig. IX. The temperature to which the bath was tested was 250°, which is as high as a copper bath should be heated. The temperatures given in the first column are those of the copper bath, while those in the second column are the temperatures of the upper compartment. The third column gives the current; the fourth, its fall of potential within the bath; the fifth, the number of watts consumed; and the sixth, the number of hours which a kilowatt will maintain the temperatures recorded in the first and second columns.

Bath No. 1.

Temperature in copper bath.	Temperature in upper compartment.	Current. Amperes.	Fall in potential. Volts.	Watts.	Hours per kilowatt.
100°	48°	1.73	15.9	27.5	36.36
125°	58°	2.10	18.8	39.48	25.58
150°	65°	2.50	21.4	53.50	18.69
175°	72°	2.77	23.2	64.26	15.56
200°	85°	3.16	25.5	80.58	12.41
225°	96°	3.48	27.0	93.96	10.75
250°	106°	4.07	29.2	118.84	8.41

Bath No. 2 differed from No. 1 only in that a stove of the kind represented in Fig. X. was used. It was tested between 150° and 258°.

Bath No. 2.

Temperature in copper bath.	Temperature in upper compartment.	Current. Amperes.	Fall in potential. Volts.	Watts.	Hours per kilowatt.
150°	73°.0	1.20	40.3	48.36	20.67
175°	83°.5	1.39	44.5	61.85	16.10
200°	95°.0	1.61	49.0	78.89	12.60
225°	104°.5	1.89	51.5	97.33	10.20
258°	111°.0	2.53	50.0	126.50	7.90

The cost of keeping the baths Nos. 1 and 2 at the temperatures given in the tables is very small. It will depend, of course, upon the price paid for the electricity, but even at the extreme current prices per kilowatt, the heating of such baths by electricity is more economical than heating them by gas. In addition to the cost of the source of the heat, we have to consider, in a problem of this kind, the relative destructive effects of the two methods upon the copper-baths; and, here again, there is a considerable advantage in favor of the use of electricity rather than gas. The electricity used in this institution is produced at an expense of 2.5 cents per kilowatt. This estimate covers interest on cost of plant, an allowance of 10 per cent for deterioration of machinery and building, average expense of current repairs, labor, and fuel. At 2.5

cents per kilowatt, the cost of maintaining bath No. 1 for a day of eight hours is: at 100°, 0.55 cent; at 125°, 0.78 cent; at 150°, 1.07 cents; at 175°, 1.29 cents; at 200°, 1.61 cents; at 225°, 1.86 cents; and at 250°, 2.38 cents. There must be added, of course, the losses due to the external resistance which is inserted in the circuit for purposes of control, but these need not be large if the conductivity of the stoves is regulated with reference to the voltage of the currents which must be used.

Where electricity is employed as the source of heat, baths made of soapstone would be more serviceable than are the copper ones in ordinary use. The former would be more cleanly and durable than the latter and could be heated to higher temperatures. According to some preliminary estimates in the hands of the authors, the first cost of baths of soapstone would be only slightly greater than of baths of copper.

A new graphite stove, when first used in its bath, should be made to maintain for several hours a somewhat higher temperature than the highest for which it was designed before any calibration of the bath is undertaken. The resistance at any given lower temperature is thereafter fairly constant. In any subsequent use of the bath, the current should never be allowed to exceed that which was employed in the preliminary heating.

Graphite, in quantities sufficient for heating by the current, may be made to adhere to a smooth surface like that of porcelain or soapstone by mixing with it a small amount of soap, and the temperature which such a covering will sustain without any marked alteration of conductivity is quite surprising. A quantity of finely pulverized electrotyping graphite was made into a thick paste by mixing it with a small amount of a concentrated solution of soap, and with this mixture, a porcelain tube, for use in the bath represented in Fig. XII., was prepared. The data obtained in testing the tube are given in the table which follows:

Porcelain Tube.

Temperature.	Current. Amperes.	Fall of potential. Volts.	Watts.	Hours per kilowatt.
150°	1.54	28.5	43.89	22.8
175°	1.74	31.7	55.66	17.9
200°	1.96	35.6	69.77	14.3
225°	2.07	37.4	77.42	12.9
250°	2.34	42 0	98.28	10.2
275°	2.59	45.0	116.55	8.6
300°	2.79	49.2	137.27	7.3
355°	3.38	55.3	186.91	5.3

Conducting surfaces made from the mixture of graphite with soap are not as satisfactory as those made from the stove polish we have used. They are more easily injured by scratching, and it is more difficult to secure a uniform distribution of the former than of the latter material.

For baths in which higher temperatures are to be kept than can safely be produced by a graphite stove, we employ the arrangement shown in Fig. XIV., in which the resistance of

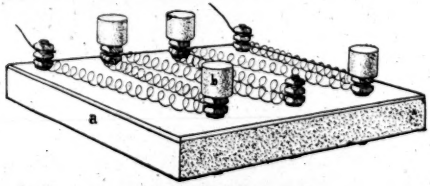


Fig. XIV.

small platinum wire is utilized to generate the heat. *a* is a soapstone block of any size to suit the dimensions of the bath, with bolts near two opposite sides, which serve to fix the coils in their places and for the attachment of the wires of the circuit. Four of the bolt ends are covered with the soapstone caps *b*. The purpose of the caps will be made apparent by an inspection of Fig. XI. The length and size of the platinum wire are made to suit the conditions which are to be met—the size of the bath, the temperature to which it is to be heated, the voltage of the available source of current, etc. In the fur-

nace shown in the figure, the wire is No. 32 (B & S gauge) and 8 feet long. To prepare the wire, it is straightened, heated to redness by the current, and then wound on a threaded steel rod of the proper diameter. Such furnaces may, of course, be used in the place of the graphite stoves previously described, and the following table gives the data which were obtained while testing one of them in a bath arranged as shown in Fig. XI., except that the shelf *f* in this case was perforated so as to permit free circulation of air between the upper and lower compartments:

Bath with Platinum-wire Stove.

Temperature in copper bath.	Temperature in upper compartment.	Current. Amperes.	Fall of potential in bath. Volts.	Watts.	Hours per kilowatt.
100°		1.08	28.5	30.8	30.5
125°	72°	1.24	34.9	43.3	23.1
150°	80°	1.4	41.8	58.5	17.1
175°	89°	1.6	51.0	81.6	12.3
200°	110°	1.77	59 8	105.9	9.5
225°	125°	1.89	66.4	125.5	8.0
250°	144°	2.0	73.0	146.0	6.9

Fig. XV. shows a bath with platinum stove which was constructed for the purpose of heating rather large vessels to any temperature up to 500°. The heating coils of the stove *a* contain about 16 feet of No. 26 platinum wire; *b* is a terra cotta cylinder like those used in chimneys for stove pipes; *c* is a sheet-iron cylinder, which is covered inside and outside with asbestos paper; *d* and *d* are covers of asbestos board; *e* is a terra cotta receptacle such as is used for flower pots; *f* is sand in which the stove and the lower ends of *b* and *c* are embedded. The dimensions of the free heated space within the bath are 250 and 175 mm. For the sake of cleanliness and of improved appearance, *e*, *c*, *d*, and the outside of *b* are covered with aluminium paint. With temperatures within up to 300° it is safe to surround the outer cylinder *c* with woolen material, or better, with a thick pad made of hair. When higher temperatures are to be maintained, we employ, in place of the pad, a wooden cylinder with an internal diameter equal to the

extreme width of the base *e*, and cover it with a strip of

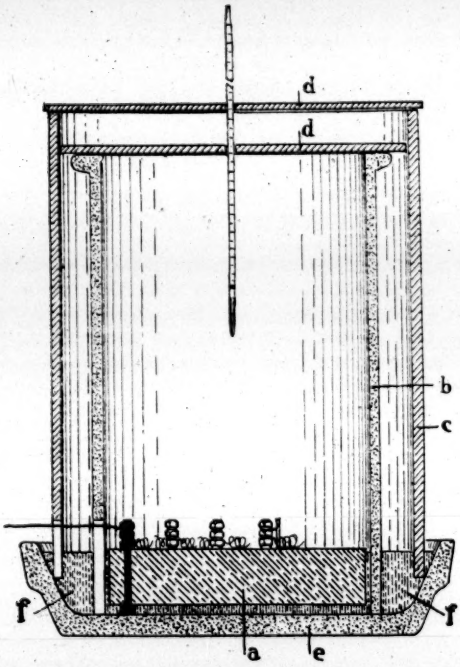


Fig. XV.

woolen cloth. A test of this bath to 400°, with the thermometer bulb located in the center of the heated space, gave the following data:

Temperature.	Current. Amperes.	Fall of potential. Volts.	Watts.	Hours per kilowatt.
100°	2.08	20.7	43.06	23.22
125°	2.20	23.0	50.60	19.76
150°	2.45	28.0	68.60	14.58
175°	2.70	32.3	87.21	11.47
200°	2.85	35.7	100.75	9.92
225°	3.04	40.8	124.03	8.06
250°	3.09	43.0	132.87	7.53
275°	3.29	48.5	159.57	6.27
300°	3.50	53.5	177.25	5.64
350°	3.73	61.0	227.53	4.40
400°	4.0	68.0	272.00	3.67

We have not tested the bath beyond 400° except to determine that, with a current pressure of 110 volts, its temperature rises above 500°.

Arrangements like that just described are an effective substitute for all of the oil and paraffin baths which give so much offense in the laboratory, and, like all electrically heated baths, they have the great advantage that, with a current of constant voltage, they can be regulated with a high degree of precision.

The foregoing are only types of the numerous electrically heated baths which we have devised for use in the laboratory, but they will suffice to illustrate both the practicability and the economy of substituting electricity for gas in many laboratory operations.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON PHENYLMALONIC NITRILE.

[PRELIMINARY PAPER.]

BY JOHN C. HESSLER.

A previous paper, entitled "On Alkyl Malonic Nitriles and Their Derivatives,"[1] described the preparation and properties of ethylmalonic and benzylmalonic nitriles and their sodium and silver salts. A study of the decomposition of these salts made it appear very probable that the metal is bound to nitrogen. It was hoped that further evidence re-

[1] This JOURNAL, 22, 169.

garding the linking of the metal in substances of this class might be obtained from the salts of phenylmalonic nitrile, consequently the preparation of this substance was attempted.

Phenylmalonic nitrile was made from phenylcyanacetamide, which, in turn, was prepared from phenylcyanacetic ether.

Preparation of Phenylcyanacetic Ether.

The method used for preparing phenylcyanacetic ether was a condensation of benzyl cyanide with carbonic acid ethyl ester by means of sodium.

The carbonic ether was made from Kahlbaum's chlorcarbonic ether and alcoholic sodium ethylate. It boiled at 125° C. The benzyl cyanide used was Kahlbaum's preparation. It boiled at 226° C.

Ten and nine-tenths grams of sodium, in wire form, were put into a solution of 56 grams of carbonic ether (one gram-molecule) in 350 cc. of absolute ether. There was only a very slight action. Then 56 grams (the theoretical amount) of benzyl cyanide were added in several portions. Hydrogen began to escape at once, and the sodium was colored golden-yellow. The temperature soon rose to the boiling-point of the ether; consequently the flask was kept cool (by means of running water) until the greater part of the sodium had gone into solution. The mixture was then allowed to stand for about twelve hours. The reaction-product separated out as a yellow solid. The supernatant ether was brown.

Dilute sulphuric acid was now added, and the yellow solid went into solution. The ethereal layer was separated, washed with water, and dried over calcium chloride. After the distillation of the ether a brown oil remained. This was distilled at reduced pressure (25 mm.) with the following result:

Fraction.	Temperature.	Weight. Grams.
1	Up to 115° C.	3.0
2	115° to 150°	10.1
3	150° to 170°	15.6
4	170°	22.5
5	170° to 180°	19.8

Three grams of tar remained in the distilling-flask.

A redistillation of fractions 2 to 5, inclusive, gave 50 grams of a practically colorless oil boiling at 160° to 170° (chiefly at 164° to 165°) at 17.5 mm. A portion was specially purified for analysis, and proved to be phenylcyanacetic ether.

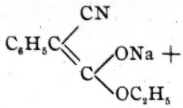
I. 0.1778 gram substance gave 0.4561 gram CO_2 and 0.0969 gram H_2O.

II. 0.2494 gram substance gave 16.7 cc. N_2 at 18°.5 C. and 741.1 mm.

	Calculated for $C_{11}H_{11}O_2N$.	Found. I.	II.
C	69.84	69.96	....
H	5.82	6.06	....
N	7.41	....	7.55

The formation of phenylcyanacetic ether is probably represented by the equation

$$C_6H_5CH_2CN + CO(OC_2H_5)_2 + Na \rightarrow$$



$$+ HOC_2H_5 + H.$$

The lower-boiling fractions (1 and 2) consisted chiefly of carbonic ether and benzyl cyanide. That the reaction is not complete is probably due to the fact that some of the sodium reacts with the alcohol formed in the condensation.

Properties.—Phenylcyanacetic ether is a colorless oil insoluble in water, but readily miscible with organic solvents. It boils at 165°.5 C. at 20 mm. At the ordinary pressure it boils at 275° C. with only slight decomposition. The specific gravity of the substance is 1.09 at 22° C. (Westphal).

Phenylcyanacetic ether is not affected by cold, dilute acids, but it dissolves readily in aqueous alkalies. If the alkaline solution is acidified at once the ester may be recovered, but after standing some hours it is saponified to phenylcyanacetic acid (*q. v.*). The ester dissolves readily in ammonia solution, giving, after some time, crystals of phenylcyanacetamide.

Sodium Salt of Phenylcyanacetic Ether.—An absolute ethereal solution of phenylcyanacetic ether reacted vigorously with sodium, forming the sodium salt. This separated as a white powder. After twenty-four hours it was filtered off, washed with absolute ether, dried for five minutes on a clay plate, and then *in vacuo* over sulphuric acid and caustic potash.

I. 0.2708 gram substance gave 0.0861 gram Na_2SO_4.
II. 0.3246 gram substance gave 0.106 gram Na_2SO_4.

	Calculated for $C_{11}H_{10}O_2NNa$.	Found. I.	II.
Na	10.9	10.3	10.58

The sodium salt of phenylcyanacetic ether is a hygroscopic substance. Its dilute alcoholic solution gives a white precipitate with silver nitrate solution, but the precipitate soon turns black.

Preparation of Phenylcyanacetamide.

Phenylcyanacetic ether (42.2 grams) was treated with 49 grams of concentrated ammonia water. The ester went entirely into solution, and the mixture became warm and somewhat colored. After several hours the mixture was practically solid. The crystals of the amide were then filtered off, washed with water, and dried on a clay plate. The weight obtained was 24.5 grams, instead of 35.7 grams, the theoretical amount.

Properties.—Recrystallized from absolute alcohol, the amide melts at 147° C. It is practically insoluble in cold water, very difficultly soluble in ether, and only slightly soluble in cold alcohol. In hot absolute alcohol it dissolves readily, separating from the cooled solution in large crystals.

Phenylcyanacetamide dissolves readily in cold 10 per cent caustic soda solution, giving off ammonia. The sample used for analysis was recrystallized from absolute alcohol and dried *in vacuo* over sulphuric acid.

0.155 gram substance gave 0.3841 gram CO_2 and 0.0719 gram H_2O.

	Calculated for $C_9H_8ON_2$.	Found.
C	67.5	67.58
H	5.0	5.15

Preparation of Phenylmalonic Nitrile.

Eight grams of phenylcyanacetamide and 4.2 grams of phosphorus pentachloride were mixed in an Anschütz flask. The flask was exhausted to 23 mm. and then heated to 120° to 125° C. in a metal-bath. A reaction began almost at once and continued for about ten minutes. When the mixture was in quiet fusion, the temperature of the bath was raised until the phenylmalonic nitrile distilled over. It collected in the side tube of the flask as a liquid, but soon solidified. The weight of the crude product was 4.2 grams, *i. e.*, about 60 per cent of the theoretical amount. Much tar remained in the distilling-flask. The proportions of phenylcyanacetamide and phosphorus pentachloride used correspond to 5 molecules of the amide and 2 of the pentachloride.[1]

A portion of the phenylmalonic nitrile was crystallized from dilute alcohol and dried *in vacuo* over sulphuric acid. It melted at 68° to 69° C.

I. 0.1524 gram substance gave 0.4224 gram CO_2 and 0.0652 gram H_2O.

II. 0.1273 gram substance gave 22.6 cc. N_2 at 23° C. and 751.2 mm.

	Calculated for $C_9H_6N_2$.	Found. I.	Found. II.
C	76.06	75.59	....
H	4.22	4.75	....
N	19.72	....	19.88

Properties.—Phenylmalonic nitrile is difficultly soluble in water and in ligroin, but readily soluble in alcohol and in ether. It crystallizes from dilute alcohol in large, white crystals. It crystallizes well, also, from a mixture of ether and ligroin (40° to 60°). From the fused condition phenylmalonic nitrile crystallizes in hexagonal plates. The substance boils undecomposed at 152° to 153° C. at 21 mm.

[1] This JOURNAL, **22**, 181; Hesse: *Ibid.*, **18**, 726.

Action of Alkalies on Phenylmalonic Nitrile.

Phenylmalonic nitrile is not readily saponified, even by concentrated alkalies, and differs greatly in this respect from benzylmalonic nitrile.[1]

Eight-tenths gram of the substance was dissolved in a large excess of 10 per cent caustic soda solution and left for twenty-four days. An excess of dilute sulphuric acid was then added and the resulting precipitate of phenylmalonic nitrile was filtered off, washed with water, and dried on a clay plate. The substance recovered weighed 0.45 gram. It melted at 68° C. The recovered phenylmalonic nitrile was then heated to boiling with 10 per cent caustic soda for ten minutes. Not a trace of ammonia was evolved. When the solution was acidified as before, 0.38 gram of the substance was recovered.

Finally, the substance (0.38 gram) was left standing with an excess of alcoholic caustic potash for four days, and the mixture was afterwards heated to boiling thirty minutes under a reflux condenser. Water and sulphuric acid were then added, the solution was extracted with ether, and the ether extract was washed with water and dried with calcium chloride. When the ether was distilled off, 0.3 gram of phenylmalonic nitrile was recovered.

Phenylmalonic nitrile is soluble in aqueous sodium carbonate, and is extracted by it from ether solution. Aqueous solutions of phenylmalonic nitrile give precipitates with solutions of copper sulphate, mercuric chloride, and silver nitrate.

Sodium Salt of Phenylmalonic Nitrile.—Phenylmalonic nitrile (3.8 grams) was dissolved in 75 cc. absolute ether and treated with 0.8 gram (an excess) of sodium in wire form. The reaction was rather slow, but was accelerated by the addition of 1 drop of absolute alcohol. After sixteen hours the unused sodium was picked out and the precipitated sodium salt was filtered off, washed with absolute ether, and dried *in vacuo* over sulphuric acid. The yield was 4 grams, *i. e.*, about 90 per cent of the theoretical. An analysis gave the following result:

0.3055 gram substance gave 0.1347 gram Na_2SO_4.

[1] This JOURNAL, 22, 181.

	Calculated for $C_9H_5N_2Na$.	Found.
Na	14.02	14.28

The sodium salt of phenylmalonic nitrile is white when freshly made, but when left over sulphuric acid *in vacuo* for several days it becomes violet. It reacts very slowly, if at all, with methyl and ethyl iodides under ordinary conditions. The aqueous solution of the sodium salt gives back phenylmalonic nitrile when acidified. The aqueous solution also gives precipitates with solutions of barium chloride, lead acetate, copper sulphate, silver nitrate, and mercuric chloride.

An attempt to get the sodium salt from benzene solution did not succeed. Five grams of phenylmalonic nitrile, dissolved in 50 grams of benzene, were treated with 1.5 grams (an excess) of sodium wire, and left for four months. Practically no action took place, as was shown by the fact that 4.8 grams of phenylmalonic nitrile were recovered.

Silver Salt of Phenylmalonic Nitrile.—All attempts to prepare the silver salt of phenylmalonic nitrile have failed, owing to its instability. This fact is evident from the following experiments:

Six and six-tenths grams of phenylmalonic nitrile were dissolved in 200 cc. of 50 per cent alcohol, cooled in iced water, and treated with a solution of 7.9 grams (1 molecule) of silver nitrate in 50 per cent alcohol. The silver salt separated out as a white, bulky precipitate, but in a few minutes it became, first, steel-blue and then light-brown in color. It was filtered off, washed with water, and dried on a clay plate and *in vacuo* over sulphuric acid. The weight obtained was 11 grams, or practically the theoretical amount. When the product was treated with ether it was found that the ether extracted organic material. Accordingly, the residue was heated with ether five times under a reflux condenser. The residual powder had the appearance of reduced silver, but still contained organic material. This fact was shown by the ignition of two samples, after they had been dried *in vacuo*.

I. 0.7406 gram substance gave 0.6351 gram Ag, or 85.75 per cent.

II. 0.5825 gram substance gave 0.4991 gram Ag, or 85.68 per cent.

The residue was then extracted four times more with boiling ether and dried *in vacuo*. Ignition of a sample gave the following result:

0.4273 gram substance gave 0.3788 gram Ag, or 88.65 per cent.

During every ignition the solid first became dark, then lost a sharp smelling, red vapor, and finally became coal-black. Heating with the blast-lamp for a long time was necessary to make the silver residue white.

When the combined ether extracts were distilled, a gummy solid remained. This turned red in moist air and in aqueous solution. When dried on a clay plate it was found to be amorphous and almost white. The substance was dissolved in ether and the solution treated with ligroin (40° to 60°). A portion was thus precipitated. When it had been dried *in vacuo* it melted at 147° to 148°.

A second attempt, in which the phenylmalonic nitrile was first treated with the theoretical quantity of sodium hydroxide, gave the same general results. A solution of 1.42 grams of phenylmalonic nitrile in 50 per cent alcohol was treated with 10 cc. (the theory) of normal caustic soda solution and then with 1.7 grams of silver nitrate dissolved in dilute alcohol. The silver salt was precipitated, but changed as before.

0.3324 gram substance gave, on ignition, 0.1471 gram Ag.

	Calculated for $C_9H_5N_2Ag$.	Found.
Ag	43.37	44.25

The high percentage of silver was undoubtedly due to the fact that some of the organic material remained in solution in the dilute alcohol.

Boiling ether extracted from the product the same substance as was formed in the first experiment. When this substance was precipitated from ethereal solution by means of ligroin (40° to 60°), it melted as before, at 147° to 148°.

Two carbon and hydrogen determinations of different

preparations of the substance gave practically identical results. A nitrogen determination was also made.

I. 0.0791 gram substance gave 0.2225 gram CO_2 and 0.027 gram H_2O.

II. 0.1602 gram substance gave 0.4504 gram CO_2 and 0.0541 gram H_2O.

III. 0.1241 gram substance gave 21.4 cc. N_2 at 21° C. and 755.8 mm.

	Calculated for		Found.		
	$C_9H_6N_2$.	$C_9H_5N_2$.	I.	II.	III.
C	76.06	76.59	76.71	76.68	....
H	4.22	3.55	3.79	3.75	....
N	19.72	19.86	....	....	19.61

The substance burned with difficulty, and the last portions of the nitrogen came off only at red heat. This may account for the fact that the percentage of nitrogen was low.

The nature of all the substances formed when silver nitrate reacts with phenylmalonic nitrile is being investigated. The body melting at 147° to 148° seems to be only one of several products.

Phenylcyanacetic Acid.

Preparation.—Phenylcyanacetic acid was prepared by the saponification of its ethyl ester. The ester was dissolved in ether, and the solution was shaken with sodium hydroxide. After the alkaline solution had stood over night it was acidified with dilute sulphuric acid, and the separated acid was extracted with ether. There was obtained an almost colorless oil, which solidified on cooling. After it had been dried on a clay plate the solid melted at 62° to 65°.

That the substance was phenylcyanacetic acid was shown by converting it into its silver salt. Some of the crude product was dissolved in a slight excess of ammonia, and the excess was removed *in vacuo* over sulphuric acid. A solution of silver nitrate (a slight excess) was then added. The silver salt separated as a white, curdy precipitate, which soon became granular. A silver determination, by ignition, gave the following result:

0.3191 gram substance gave 0.128 gram Ag.

	Calculated for $C_9H_6NO_2Ag$.	Found.
Ag	40.29	40.11

When the crude acid, melting at 62° to 65°, was recrystallized from ether-ligroin, the melting-point was raised about 10°. After two recrystallizations from hot benzene the substance was dried *in vacuo* over sulphuric acid. It then melted sharply at 92° C.

0.1663 gram substance gave 0.41 gram CO_2 and 0.072 gram H_2O.

	Calculated for $C_9H_7O_2N$.	Found.
C	67.08	67.24
H	4.35	4.81

Properties.—Phenylcyanacetic acid is soluble in water, alcohol, ether, and hot benzene; insoluble in ligroin. When heated in a bath at 150° to 160° it decomposes, giving carbon dioxide and benzyl cyanide.

Action of Phenylmalonic Nitrile with Methyl Iodide and Alcoholic Sodium Ethylate.

Phenylmethylcyanacetimido Ethyl Ester.—Two grams of phenylmalonic nitrile in absolute alcoholic solution were treated with 0.32 gram (1 atom) of sodium, also dissolved in absolute alcohol. Three grams of methyl iodide (1.5 molecules) were then added. The temperature of the mixture rose to 32° C. After forty minutes the alcohol was distilled off, water was added, and the separated oil was extracted with ether. The ether solution was washed with sodium hydroxide solution and with water, and was dried with calcium chloride. Distillation of the ether left a colorless oil, which was distilled *in vacuo*. The yield was 2.4 grams, or practically theoretical.

An analysis gave the following results:

I. 0.2075 gram substance gave 0.5428 gram CO_2 and 0.1304 gram H_2O.

II. 0.1947 gram substance gave 24.5 cc. N, at 18° C. and 740.3 mm.

	Calculated for $C_{12}H_{14}ON_2$.	Found. I.	II.
C	71.29	71.34	....
H	6.93	6.99	....
N	13.86	....	14.21

The imido ether is a faintly aromatic oil boiling at 152° to 153° at 16 mm. and at 158° to 159° at 22 to 23 mm. Its specific gravity is very nearly 1.06 at 23° C. The substance is insoluble in water, but dissolves readily in alcohol and in ether. The alcoholic solution instantly gives a precipitate of ammonium chloride when treated with concentrated hydrochloric acid.

Action of Phenylmalonic Nitrile with Benzyl Chloride and Alcoholic Sodium Ethylate.

Phenylbenzylmalonic Nitrile.—Two grams of phenylmalonic nitrile, dissolved in absolute alcohol, were treated with 0.32 gram (1 atom) of sodium, also in alcoholic solution, and with 2.5 grams (an excess) of benzyl chloride. The temperature of the mixture rose, and sodium chloride separated out. After the mixture had been heated under a reflux condenser for thirty minutes the alcohol was distilled off and the residue was treated with water and extracted with ether. The ethereal solution was washed with caustic soda solution and dried with calcium chloride. Evaporation of the ether left phenylbenzylmalonic nitrile. The crude substance (3.5 grams) was crystallized from ether-ligroin and from absolute alcohol. It melted in each case at 97° to 98°.

0.17 gram substance gave 0.5154 gram CO_2 and 0.0841 gram H_2O.

	Calculated for $C_{18}H_{18}N_2$.	Found.
C	82.76	82.68
H	5.17	5.49

Phenylbenzylmalonic nitrile crystallizes from ether-ligroin in long needles grouped in feathery masses. It is easily soluble in ether and in alcohol, but practically insoluble in ligroin and in water. It is not affected by aqueous alkalies, even at 100° C.

Phenylbenzylcyanacetic Ethyl Ester.—Five and seven-tenths grams of phenylcyanacetic ether, in 20 cc. of absolute alcohol, were treated with 0.7 gram (1 atom) of sodium in 25 cc. of absolute alcohol. The temperature rose and the mixture became red. Then 3.8 grams (1 molecule) of benzyl chloride were added. The temperature rose still more, and sodium chloride separated out slowly. The mixture was heated under a reflux condenser for three hours, the sodium chloride filtered off, and the alcoholic solution distilled. There were obtained 7.4 grams of an oil boiling at 231° to 233° at 32 mm. and at 216° to 217° at 16 mm. An analysis resulted as follows:

I. 0.186 gram substance gave 0.5268 gram CO_2 and 0.1076 gram H_2O.

II. 0.5512 gram substance gave 24.4 cc. N_2 at 15°.5 C. and 757.5 mm.

	Calculated for $C_{15}H_{17}ON_2$.	Found. I.	II.
C	77.42	77.24	....
H	6.09	6.43	....
N	5.02	....	5.17

Phenylbenzylcyanacetic ether is a thick, colorless liquid having the sp. gr. 1.13 at 22° C. In a freezing-mixture and in an outside room at winter temperature it became so viscous that it could not be poured, but it would not crystallize. The substance is insoluble in water and is not affected by aqueous alkalies.

The study of phenylmalonic nitrile and its derivatives is being continued in this laboratory.

CHICAGO, January 25, 1904.

Contributions from the Sheffield Laboratory of Yale University.

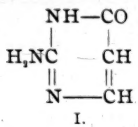
CXV.—RESEARCHES ON PYRIMIDINES. SYNTHESIS OF 2-AMINO-5-METHYL-6-OXYPYRIMIDINE.

[SIXTH PAPER.]

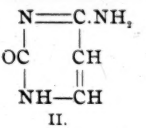
BY TREAT B. JOHNSON AND SAMUEL H. CLAPP.

In a previous paper from this laboratory, Wheeler and

Johnson[1] described the two monoaminooxypyrimidines which can give uracil on hydrolysis, *viz.*, 2-aminooxypyrimidine (Formula I.), and 2-oxy-6-aminopyrimidine or cytosine (Formula II.):

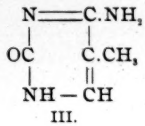


I.

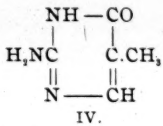


II.

In a similar manner the two monoaminomethylpyrimidines which could give thymine on hydrolysis are, *viz.*, 2-oxy-6-amino-5-methylpyrimidine (Formula III.) and 2-amino-6-oxy-5-methylpyrimidine (Formula IV.):



III.



IV.

Wheeler and Johnson[2] in a recent paper have described 2-oxy-6-amino-5-methylpyrimidine (Formula III.) and have shown that it is more or less readily converted into thymine on hydrolysis.

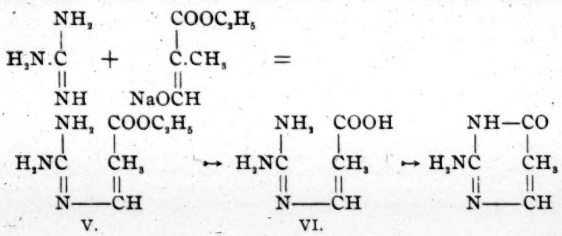
We will describe in this paper the second monoaminomethylpyrimidine (Formula IV.), which theoretically could give thymine on hydrolysis, *viz.*, 2-amino-5-methyl-6-oxypyrimidine. We have synthesized this aminopyrimidine by condensing guanidine with the sodium salt of formylethylpropionate. We have not only been able to obtain the pyrimidine base which we desired, but have also succeeded in isolating intermediate products in the reaction. These have given us a more thorough insight into the mechanism of these pyrimidine condensations.

We find, namely, that in this condensation there are three steps in the reaction—first a condensation of guanidine with

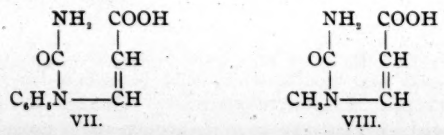
[1] This JOURNAL, **29**, 492 (1903).

[2] *Ibid.*, **31**, 592 (1904).

the formyl group of the sodium formylethylpropionate giving an acrylic ester (Formula V.), then a saponification of the acrylic ester to the free acid (Formula VI.), and finally a condensation to the pyrimidine with loss of a molecule of water :



Under the conditions by which we worked we did not observe the formation of the intermediate guanidineacrylic ester, but have evidence of its existence because of the fact that we have been able to isolate the intermediate guanidinemethylacrylic acid. Müller[1] has described two substituted acrylic acids that are analogous to our intermediate acid. He found that phenylurea and methylurea readily condensed with oxalethylacetate, giving a phenyluracilcarboxylic ester and methyluracilcarboxylic ester. By dissolving these two esters in alkali and treating with strong hydrochloric acid they were decomposed into uramidoacrylic acids (Formulas VII. and VIII.) :



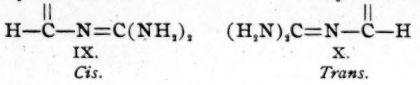
Behrend,[2] in his synthesis of methyluracil from acetoacetic ester and urea, was able to isolate an intermediate uramidocrotonic ester, but was unable to isolate the free acid from its

[1] J. prakt. Chem., **56**, 475.
[2] Ann. Chem. (Liebig), **229**, 8.

sodium or potassium salt on account of the ease with which it condensed to the pyrimidine.

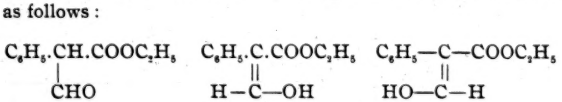
We, furthermore, have made the interesting observation that our intermediate α-methyl-β-guanidineacrylic acid is capable of existing in two isomeric modifications. One acid melts at 331° to 332° C. with violent effervescence; the other at 318° to 320° C. to a clear oil. Both acids can be converted by treatment with alkali into the 2-amido-5-methyl-6-oxypyrimidine.

It appears to us that the explanation for this interesting case of isomerism is that we are dealing with an ethylene linking, and have another case of *cis* and *trans* isomerism:



IX. *Cis.* X. *Trans.*

Wislicenus[1] was able to isolate three isomeric modifications of formylphenylethylacetate. He represented their structure as follows:



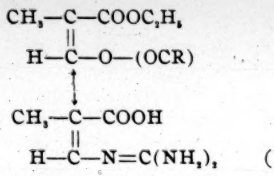
XI. XII. XIII.

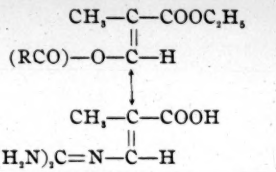
He furthermore showed that the *enol* form was capable of forming isomeric salts, which gave isomeric acyl modifications when treated with acyl chlorides.

In a later paper Wislicenus and Bindemann[2] showed that analogous acyl modifications could be obtained from the sodium salt of formylethylacetate. Finally, Wislicenus[3] extended his investigations to the sodium salt of formylethylpropionate, which we used in our condensation, and observed that this also gave stereochemical isomers when treated with acyl chlorides. The close analogy between Wislicenus' iso-

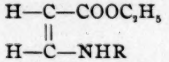
[1] Ann. Chem. (Liebig), **312**, 33.
[2] *Ibid.*, **316**, 18.
[3] *Ibid.*, **316**, 333.

mers and our modifications is shown by the following formulas:

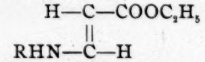




It seems probable to the writer that Pechmann's[1] isomeric derivatives which he obtained by treating the sodium salt of formylethylacetate with aniline and paratoluidine are to be explained in a similar manner:



XIV.



XV.

Erlenmeyer[2] has shown that ethyl formate can be condensed with hippuric ethyl ester by means of sodium ethylate to the sodium salt of oxymethylenehippuric ester. We have prepared this salt and find that it condenses very smoothly with pseudoethylthiourea, giving 2-ethylmercapto-5-benzoylamino-6-oxypyrimidine.

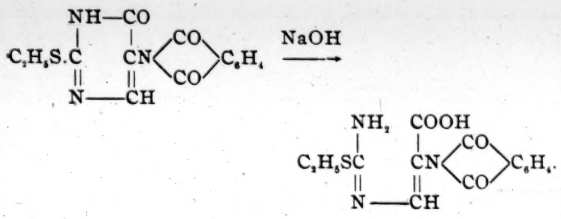
We, furthermore, have condensed ethyl formate with phthalimidoethylacetate to the sodium salt of formylphthalimidoethylacetate. We find that this salt condenses with pseudoethylthiourea with the formation of 2-ethylmercapto-5-phthalimido-6-oxypyrimidine, and an intermediate acrylic acid.

The two above pyrimidines show a most striking behavior towards alkali. 2-Ethylmercapto-5-benzoylamino-6-oxypyrimidine dissolves in alkali and is precipitated unaltered by acids, while, on the other hand, the analogous 2-ethylmercapto-5-phthalimido-6-oxypyrimidine is converted under the same conditions into the corresponding pseudoureaphthalimidoacrylic acid.[3]

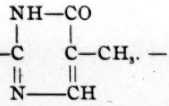
[1] Ber. d. chem. Ges., **28**, 1052.

[2] *Ibid.*, **36**, 3769.

[3] Since the above was written we have found that 2-ethylmercapto-5-benzoylamino-6-oxypyrimidine is converted by alkali into the sodium salt of the corresponding pseudoureabenzoylaminoacrylic acid. We have not succeeded in isolating the free acid.



EXPERIMENTAL PART.

2-Amino-5-methyl-6-oxypyrimidine, 

Seventy-two grams of guanidine carbonate were dissolved in the least possible quantity of cold water and mixed with 54 grams of barium hydroxide dissolved in 400 cc. of water. To this solution, filtered clear from the precipitated barium carbonate, 283 grams of crude sodium formylethylpropionate were added. After standing at ordinary temperature for about eight hours the clear solution was divided into two equal parts. One part was heated on the steam-bath for about half an hour and then neutralized with dilute sulphuric acid. A brown precipitate separated immediately and was filtered off and saved (see *trans* acid). The clear solution that remained was evaporated to dryness, then redissolved in a little warm water, and filtered from a small amount of insoluble material that was present. The pyrimidine base was then precipitated with phosphotungstic acid, the tungstic acid precipitate decomposed with barium hydroxide, and the excess of barium hydroxide removed in the usual way with carbon dioxide. On concentrating the solution that remained, and cooling, the base separated in the form of stout prisms and melted with effervescence at 320° to 321°.

The second part of the original solution was allowed to stand at ordinary temperature for two weeks. It was then neutralized with dilute sulphuric acid as before. An insolu-

ble brown precipitate was obtained as in the first part. After filtering off this insoluble precipitate we precipitated the pyrimidine base with mercuric chloride instead of phosphotungstic acid. The mercury was removed from the precipitate with hydrogen sulphide and then the base allowed to crystallize from the concentrated solution.

The yield of pure base by the two different methods of treatment was about equal (4 grams), showing that long standing does not increase to any extent the yield. The same observation was made by Wheeler and Johnson[1] in their preparation of isocytosine or 2-amino-6-oxypyrimidine.

2-Amido-5-methyl-6-oxypyrimidine crystallized from hot water in two distinct crystalline forms, stout prisms, and long, slender, needle-like prisms. It melts at 320° to 321° with violent effervescence. It does not contain water of crystallization. One hundred parts of water dissolve 0.43 part base at 25° C. A nitrogen determination gave:

	Calculated for $C_5H_7ON_3$.	Found. I.	Found. II.
N	33.60	33.68	33.91

The base was not hydrolyzed to thymine after heating in a sealed tube with 25 per cent sulphuric acid for five hours.

In a second condensation we modified our experiment in the following manner: After adding the sodium formylethylpropionate to the guanidine solution, we added a molecular proportion of sodium hydroxide (29 grams). The alkaline solution was then allowed to stand at a temperature of 40° to 50° for about ten hours, and then heated on the steam-bath for three hours. The solution was then divided into two equal parts and one part neutralized with acetic acid, the other with dilute sulphuric acid. An immediate precipitate of the *trans* acid resulted in both cases. The weight of insoluble acid obtained here was 12.2 grams.

The two filtrates were combined and precipitated with an excess of mercuric chloride. The mercury was removed in the usual way with hydrogen sulphide and the filtrate concentrated. On cooling the concentrated solution we obtained

[1] *Loc. cit.*

a mass of needle-shaped prisms mixed with stout prisms. Some of these needle-formed prisms melted at 319° to 320° to a clear oil, followed by a slow effervescence. That this body was not the same product as we obtained in our first condensation was shown by the fact that when it was mixed with the free pyrimidine the melting-point was lowered to 308°–310° (see *cis* acid). The yield of this crystalline product was 18.2 grams.

Behavior with Alkali.—The base dissolves very readily in the cold in both dilute (2 per cent) and strong (9 per cent) solutions of sodium hydroxide, and is precipitated unaltered when the alkaline solution is neutralized with carbon dioxide or dilute sulphuric acid. It separates in the form of needle-formed prisms and melts at 320° to 321° with violent effervescence. In appearance this crystalline form of the base resembles very much that of the *cis* acid. That the ring is not opened by the treatment with alkali is shown by the fact that when this body was mixed with the *cis* acid the melting-point was lowered to 307°. Furthermore, a nitrogen determination gave :

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.90

The Hydrochloride.—Some of the base was dissolved in concentrated hydrochloric acid and the solution concentrated in a vacuum. The hydrochloride separated in stout prisms. A chlorine determination agreed with the calculated for monohydrochloride :

	Calculated for $C_5H_7ON_3.HCl$.	Found.
Cl	21.98	21.73

The Picrate.—The picrate separated immediately from water in yellow, microscopic crystals. They were practically insoluble in boiling alcohol and water. After prolonged boiling with water the insoluble picrate was filtered off and analyzed for nitrogen :

	Calculated for $C_5H_7ON_3.C_6H_3O_7N_3$.	Found.
N	23.73	23.92

The Sulphate.—The sulphate crystallized from water in the form of flattened prisms or plates. A sulphur determination agreed with the calculated for an acid salt. It is interesting to note that Jaeger[1] obtained analogous acid sulphates from the isomeric 2-amido-4-methyl-6-oxypyrimidine, and from 2-amido-4,5-dimethyl-6-oxypyrimidine :

	Calculated for $C_5H_7ON_3.H_2SO_4$.	Found.
S	14.34	14.62

Platinum Chloride Double Salts.—Two characteristic platinum chloride double salts were obtained. The first was prepared by adding hydrogen platinic chloride to a cold, dilute hydrochloric acid solution of the base. It analyzed for a salt with 4 molecules of water of crystallization :

	Calculated for $(C_5H_7ON_3.HCl)_2PtCl_4.4H_2O$.	Found. I.	Found. II.
Pt	26.56	26.51	26.61

When hydrogen platinic chloride was added to a hot hydrochloric acid solution of the base and then the solution allowed to cool slowly, the platinum salt separated in thick tables and melted at 254° to 255°. A water determination and an analysis for platinum agreed with the calculated for a double platinum salt containing two molecules of water of crystallization :

0.1995 gram salt lost 0.0106 gram H_2O at 120° to 130° C.

	Calculated for $(C_5H_7ON_3.HCl)_2PtCl_4.2H_2O$.	Found.
Pt	27.99	27.76
H_2O	5.17	5.30

Trans-α-Methyl-β-guanidineacrylic Acid, $\begin{matrix} CH_3—C—COOH \\ \quad\quad\quad\quad\quad\quad \| \\ (H_2N)_2C=N—C—H \end{matrix}$.—This acid was always obtained in the condensation described above, when we neutralized the alkaline solution, preliminary to precipitating the pyrimidine base with mercuric chloride. It separated as an amorphous brown precipitate. One of the most characteristic physical properties that distinguished this acid from its *cis* modification and the pyrimidine was its insolubility in water. One hun-

[1] Ann. Chem. (Liebig), 262, 371.

dred parts of water dissolve 0.08 part acid at 25° C. It crystallized from boiling water in poorly developed prisms, and melted according to the rate of heating from 329° to 332° with violent effervescence. It possesses both acid and basic properties. A nitrogen determination gave:

	Calculated for $C_5H_8O_2N_2$.	Found.
N	29.37	29.32

In our second condensation the *trans* acid came down less pure and was mixed with a considerable amount of stout prisms. These were separated by boiling with water. After filtering and cooling, the prisms separated again and melted at 320° to 321° with effervescence. That this was the pyrimidine base was shown by the fact that when mixed with the pure pyrimidine the melting-point was not lowered. The *trans* acid was not changed to the *cis* modification or the pyrimidine after boiling in water for six hours. A nitrogen determination in the above pyrimidine, melting at 320° to 321°, gave:

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.68

Behavior with 9 Per Cent Sodium Hydroxide.—When the *trans* acid was dissolved either in the cold or warm sodium hydroxide solution, and the solution neutralized with carbon dioxide it separated in the form of stout prisms and melted at 320° to 321° with violent effervescence. That this was the pyrimidine base was confirmed by a nitrogen determination:

	Calculated for $C_5H_7ON_3$.	$C_5H_9O_2N_3$.	Found.
N	33.60	29.37	33.52

The formation of the pyrimidine from the *trans* acid was furthermore confirmed by the formation and analysis of its platinum chloride salt. It separated in the form of stout prisms and melted at 254° to 255°. When mixed with the double salt previously described as melting at 254° to 255° the melting-point was not lowered. A platinum determination gave:

	Calculated for $(C_4H_7ON_3.HCl)_2PtCl_4.2H_2O$.	Found.
Pt	27.99	27.93

Behavior with 2 Per Cent Sodium Hydroxide.—Some of the *trans* acid melting at 331° was dissolved in the cold, dilute sodium hydroxide solution. On neutralizing with dilute sulphuric acid it separated again as a brown, poorly crystallized precipitate. It was extremely insoluble in water and melted at 330° to 332° with violent effervescence. The *trans* acid was precipitated again unaltered after this treatment with dilute alkali. When mixed with the pure analyzed acid the melting-point was not lowered. This experiment is of interest because it enabled us to determine the *cis* and *trans* forms of our acid. The isomeric modification could not be precipitated unaltered from an alkaline solution.

Cis-α-Methyl-β-guanidineacrylic Acid, $\begin{matrix} CH_3—C—COOH \\ \quad\quad\| \\ H—C—N=C(NH_2)_2 \end{matrix}$.—This acid was obtained in our second condensation when we precipitated with mercuric chloride to obtain the pyrimidine base. After removing the mercury from the precipitate with hydrogen sulphide and concentrating the solution it separated with the pyrimidine base in slender, needle-like prisms. It was obtained pure by recrystallizing from hot water. It was approximately about twice as soluble in water as the pyrimidine. One hundred parts of water dissolve 0.84 part acid at 25°. The most noticeable physical property which this acid possesses is its behavior on melting. It melts at 319° to 320° to a clear oil, followed by a slight effervescence and slow decomposition. A nitrogen determination gave :

	Calculated for $C_5H_9O_2N_3$.	Found. I.	Found. II.
N	29.37	29.05	29.6

In order to be certain that we were dealing here with a second modification of the guanidineacrylic acid, and not with a modification of our pyrimidine containing water of crystallization, some of the acid was heated for one hour at 115° to 120°, and again at 140° for one hour. The body lost no weight by

this treatment, thus confirming our assumption that we had in hand an isomeric acid.

Behavior with 9 Per Cent Sodium Hydroxide.—The *cis* acid dissolved immediately in the sodium hydroxide solution. When the alkaline solution was neutralized with carbon dioxide or with dilute hydrochloric acid an asbestos-like precipitate of needle-like prisms were obtained. They melted at 319° to 321° with effervescence. When mixed with the pyrimidine (m. p. 320°) the melting-point was not lowered. When mixed with the *cis* acid (m. p. 319° to 320°) the melting-point was lowered to from 302° to 303°. That the *cis* acid had been converted into the pyrimidine was confirmed by a nitrogen determination:

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.23

Behavior with 2 Per Cent Sodium Hydroxide.—The *cis* acid that was used in this experiment melted sharply at 320° to a clear oil and analyzed for 29.05 per cent of nitrogen, calculated 29.37 per cent. It dissolved immediately in the cold, dilute sodium hydroxide solution. When the alkaline solution was neutralized with carbon dioxide or sulphuric acid the base was precipitated in needle-like prisms melting at 320° with effervescence. A nitrogen determination agreed with the calculated for the pyrimidine:

	Calculated for $C_5H_7ON_3$.	Found.
N	33.60	33.43

Acetic acid also precipitated from an alkaline solution of the *cis* acid, the pyrimidine melting at 320°.

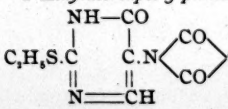
Condensation of Ethyl Formate with Phthalimidoethylacetate.—This condensation was effected by suspending the phthalimidoethylacetate in benzene or ether with the calculated amount of sodium and adding slowly the ethyl formate. The condensation was not smooth, and after standing for several hours, with occasional shaking, much phthalimidoethylacetate remained unaltered. From 50 grams of phthalimidoethylacetate about 50 grams of crude sodium salt were obtained.

This sodium salt is exceedingly unstable in aqueous solution. Some of the salt was dissolved in water and then filtered. When this clear salt solution was allowed to stand for several hours at ordinary temperature it gradually deposited a crystalline solid. This crystallized from alcohol in needle-like prisms and melted at 111°. It proved to be unaltered phthalimidoethylacetate. When the filtered solution was acidified with hydrochloric acid no further precipitation took place.

On the other hand, when a solution of the sodium salt was immediately acidified with hydrochloric acid a semisolid precipitate was obtained. It was insoluble in hot water. It dissolved in cold alcohol with the exception of a small amount of white, crystalline material. This insoluble product crystallized from hot alcohol in needles and melted at 193° to 194°. It was soluble in alkali to a yellow solution. This body was identified as 4-oxyisoquinoline-3-carboxylic ethyl ester, which was obtained by Gabriel and Colman[1] by heating phthalimidoethylacetate with sodium ethylate and alcohol at 100°. A nitrogen determination gave:

	Calculated for $C_{12}H_{11}O_4N$.	Found.
N	6.00	6.21

When the above alcoholic extract was evaporated to dryness a thick syrup was obtained which immediately solidified on cooling. It crystallized from alcohol in prisms and melted at 111° to 112°. It was identified as phthalimidoethylacetate.

2-Ethylmercapto-5-phthalimido-6-oxypyrimidine,  —This pyrimidine was obtained by condensing pseudoethylthiourea in aqueous solution with the sodium salt of formylphthalimidoethylacetate. Six and two-tenths grams of the crude salt were treated with 160 cc. of water and filtered from the unaltered phthalimidoethylacetate. To the clear solution was then added an aqueous solution of

[1] Ber. d. chem. Ges., 33, 983.

the pseudourea, that was prepared by mixing a solution of 36 grams of the hydrobromide with 11 grams of potassium hydroxide. The resulting mixture was then allowed to stand at ordinary temperature for one hour, and then heated on the steam-bath. Mercaptan was evolved in large amount, and on prolonged heating the solution assumed a dark-green color. A crystalline precipitate finally began to separate from the hot solution when the mixture was removed from the bath and allowed to cool. This crystalline body proved to be phthalimidoethyl-acetate. On acidifying the solution with sulphuric acid a thick, gummy precipitate was obtained, which was purified by boiling with water and animal charcoal. It crystallized from alcohol in rhombic plates and melted at 230° to 231° to a yellow oil. It gave a strong test for sulphur. A nitrogen determination gave:

	Calculated for $C_{14}H_{11}O_3N_2S$.	Found.
N	13.95	14.3

When the above pyrimidine was dissolved in alkali and then acidified with dilute hydrochloric or sulphuric acid a white, crystalline precipitate was immediately obtained. It crystallized from 50 per cent alcohol and melted with violent effervescence at 130° to 131°, then solidified again in the hot bath, and did not melt again until 229° to a clear, yellow oil. It gave a strong test for sulphur. A nitrogen determination agreed with the calculated for α-phthalimido-β-pseudoethyl-thioureaacrylic acid,

$$C_6H_4(CO)_2N{-}C(COOH){=}CH.N{=}C(SC_2H_5){-}NH_2:$$

	Calculated for $C_{14}H_{13}O_4N_3S$.	Found.
N	13.16	13.26

This same acid was obtained in the above condensation when the acid filtrates were allowed to stand. It separated in small prisms and was purified by crystallizing from alcohol. When the acid was heated above its melting-point in an oil-bath it immediately decomposed with loss of a molecule of water, giving the pyrimidine derivative melting at 231°.

When mixed with the pyrimidine the melting-point was not lowered.

Sodium Salt of Oxymethylenehippuric Ethyl Ester, $NaO-CH=C<^{NH.COC_6H_5}_{COOC_2H_5}$.—This salt was used by Erlenmeyer[1] in his synthesis of serine and cystine. He gives no directions for preparing the salt, but states that he obtained it by condensing ethyl formate with hippuric ethyl ester in presence of sodium ethylate.

We have prepared the salt by condensing hippuric ethyl ester with ethyl formate in benzene in the presence of metallic sodium. The condensation is very slow. From 25 grams of hippuric ester we obtained 35 grams of the crude salt.

2-Ethylmercapto-5-benzoylamino-6-oxypyrimidine, $C_2H_5S.C(=N-CH)-CNH.COC_6H_5$ (NH—CO).—Thirty-five grams of the above sodium salt were dissolved in cold water and combined with an aqueous solution of pseudoethylthiourea. Only 0.5 molecular proportion of pseudourea was used in this reaction, or 13 grams of the hydrobromide, which were neutralized with 4 grams of potassium hydroxide. The mixture was allowed to stand at ordinary temperature for forty-eight hours. No odor of mercaptan was noticeable. When the mixture was examined a large amount of crystalline material had separated from the aqueous solution. This crystallized from alcohol in needles and melted at 238° to 239° to a yellow oil. It gave a strong test for sulphur and did not decompose when heated to 260°. A nitrogen determination gave:

	Calculated for $C_{13}H_{13}O_2N_3S$.	Found.
N	15.27	15.50

The pyrimidine was soluble in alkali and was precipitated unaltered by hydrochloric acid.

[1] Ber. d. chem. Ges., **36**, 3769; **38**, 2720.

When the alcoholic filtrates from the above purification were combined and evaporated to dryness an oil was obtained which finally solidified. It was identified as unaltered hippuric ester.

More of the above pyrimidine was obtained by acidifying the original solution after filtering off the crystalline material that had separated. It was precipitated as a semisolid, which quickly solidified on cooling. It crystallized from alcohol in needles and melted at 238° to 239°.

NEW HAVEN, CONN., Feb. 24, 1904.

Contributions from the New York Agricultural Experiment Station.

VIII.—CHEMICAL CHANGES IN THE SOURING OF MILK.

BY LUCIUS L. VAN SLYKE AND EDWIN B. HART.

In the ordinary souring of milk two phenomena are familiar: First, the formation of acid, resulting in giving milk a sour taste and a characteristic odor, and, second, the curdling or coagulation of the milk-casein. The formation of lactic acid in the souring of milk from milk-sugar by means of acid-forming organisms has been well known for years, but the character of the action causing coagulation of milk-casein has not been satisfactorily established, though explained in various ways.

Among the explanations that have been offered to indicate what takes place when an acid precipitates milk-casein, we will call attention to two. The first explanation was offered by Scheele in 1780, who was the pioneer in the study of lactic acid. He expressed the view that the precipitate formed by treating milk with an acid is a compound produced by the union of the acid with milk-casein. In 1865, Millon and Commaille[1] carried on some experiments which led them to the same view. In 1893 Timpe[2] made a study of the souring of milk and stated that a given amount of casein unites with a definite quantity of lactic acid to form a definite chemical compound. Owing to the variation in views expressed by

[1] Compt. rend., **59**, 301 (1865).

[2] Arch. Hyg., **18**, 1 (1893).

different workers, Hammarsten[1] took up the question and concluded as a result of his work that there was no ground for believing that a chemical combination takes place between casein and the acid used to precipitate it. He based his statement mainly on the fact that by rubbing for several days in a mortar with different portions of water, a precipitate formed by casein with an acid, he was able to remove the acid so completely that the remaining precipitate gave no test for the acid. With the more recent knowledge we have of the looser forms of chemical combination common to proteids and the tendency of such compounds to dissociate under conditions less severe than those used by Hammarsten, his work cannot be regarded as settling the question in such an absolute manner as he indicates. According to Hammarsten,[2] milk-casein contains calcium phosphate in combination, and the treatment with acid removes the calcium phosphate, which results in precipitating casein. This view in somewhat modified forms has been held by Eugling,[3] Schaffer,[4] and Söldner.[5]

In this JOURNAL (**28**, 424–430 (1902)) we called attention, in a preliminary way, to the fact that we had isolated two different compounds formed by casein when treated with lactic acid, one of which we were led to regard as casein monolactate and the other as casein dilactate. Both compounds are insoluble in water. The monolactate is completely soluble at about 55° C. in a 5 per cent solution of sodium chloride, while the dilactate is practically insoluble in this solvent. It appears that Hammarsten really prepared these compounds but did not recognize what they were or their relations to each other. He says:[6] "When we carefully precipitate a very dilute solution of casein with a very dilute acid, there is formed a loose precipitate, which dissolves completely in sodium chloride to an opalescent solution." He adds that

[1] Maly Jahresber. Thierchemie, **7**, 160 (1877).
[2] *Ibid.*, **4**, 135 (1874).
[3] Landw. Versuchs.-Stat., **31**, 392 (1885).
[4] Landw. Jahrb. d. Schweiz, **1**, 33 (1887).
[5] Landw. Versuchs.-Stat., **35**, 351 (1889).
[6] Maly Jahresber. Thierchemie, **7**, 163 (1877).

when too much acid is used a precipitate is formed that is insoluble in sodium chloride solution.

We are still engaged in making a more complete study of the chemical relations of acids to casein, the final results of which will be published later. By our further study we have been able to prepare these compounds under more complete control. Some of our more recent results indicate that it may be necessary to modify to some extent the interpretation of our previous results. While many facts favor the view that there is a direct combination between the proteid and acids, other facts are not in full harmony with this position. We hope to obtain data in the near future which will furnish us a satisfactory basis for reaching definite settled conclusions in regard to this question, which has been so long a troublesome and difficult problem. Until our present interpretation of our results has been clearly shown to be inconsistent with the facts previously ascertained by us, we shall continue tentatively to speak of the compounds in question as mono- and di-salts of casein and paracasein.

It is our purpose in this paper to present the results of some recent work done to show the amounts of the casein monolactate and dilactate formed in the usual souring of milk, together with the results of a simultaneous study of some of the conditions under which the sugar in milk is changed into lactic acid.

In one set of experiments made in our study, we placed some fresh separator skim-milk in an Erlenmeyer flask, stoppered with a plug of cotton. This was allowed to stand at room temperature, and samples were taken from this flask for examination from time to time. In the first experiment the room temperature varied from 18° to 24° C.; in the second from 21° to 27° C. In another set of experiments we used 3000 cc. of pasteurized separator skim-milk, to which had been added 50 cc. of sour milk to hasten the souring. We placed in each of 14 cotton-stoppered flasks 100 cc. of this milk and allowed one lot (No. 3) to stand at a temperature of 15°.5 to 21° C., and another lot (No. 4) at 21° to 27° C. In these experiments (3 and 4) we used the contents of one flask

Table Showing Chemical Changes in the Souring of Milk.

No. of experiment.	Age of milk when analyzed. Hours.	Amount of milk-sugar in milk. Per cent.	Amount of milk-sugar changed. Per cent.	Amount of lactic acid in milk. Per cent.	Proportion of sugar in milk changed. Per cent.	Nitrogen in milk in soluble form. Per cent.	Casein in form of monolactate. Per cent.	
1	Fresh	5.15	....	....	....	....	....	
2	"	5.58	....	....	....	....	....	
3	"	5.08	....	0.187	....	....	....	
4	"	5.08	....	0.187	....	....	....	
1	8	4.53	0.62	....	12.04	....	....	
2	8	5.25	0.33	....	5.91	....	....	
3	8	4.53	0.55	0.011[1]	10.83	....	....	
4	8	4.32	0.76	0.081[1]	14.96	....	....	
1	24	4.25	0.90	....	17.48	....	....	
2	24	4.42	1.16	....	20.80	21.19	12.70	Coagulated
3	24	4.00	1.08	0.506[1]	21.26	....	....	
4	24	3.79	1.29	0.776[1]	25.40	....	....	Coagulated
3	26	3.92	1.16	0.596[1]	28.43	....	....	Coagulated
1	29½	3.88	1.27	....	24.66	17.44	14.43	Coagulated
1	32	3.71	1.44	....	28.00	22.61	13.18	
2	32	4.20	1.38	....	24.73	22.68	11.50	
3	32	3.86	1.22	0.740[1]	24.00	....	....	
4	32	3.76	1.32	0.848[1]	26.00	....	....	

[1] Amount of lactic acid less the amount of acid in the fresh milk.

Table Showing Chemical Changes in the Souring of Milk (Continued).

No. of experiment.	Age of milk when analyzed.	Amount of milk-sugar in milk.	Amount of milk-sugar changed.	Amount of lactic acid in milk.	Proportion of sugar in milk changed.	Nitrogen in milk in soluble form.	Casein in form of monolactate.
	Hours.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	48	3.70	1.45	....	28.10	22.80	10.20
2	48	4.18	1.40	....	25.10	21.19	8.61
3	48	3.79	1.29	0.821[1]	25.40	....	....
4	48	3.76	1.32	0.848[1]	26.00	....	....
1	72	3.65	1.50	....	29.13	24.14	8.00
2	72	4.13	1.45	....	26.00	21.38	8.61
3	72	3.76	1.32	0.839[1]	26.00	....	....
4	72	3.72	1.36	0.857[1]	26.77	....	....
1	96	3.66	1.49	....	28.93	23.95	6.70
2	96	4.07	1.51	....	27.06	22.87	6.00
3	96	3.70	1.38	0.875[1]	27.16	....	....
4	96	3.69	1.39	0.884[1]	27.36	....	....
2	120	4.07	1.51	....	27.06	22.68	5.74
3	120	3.62	1.46	0.893[1]	28.74	....	....
4	120	3.64	1.44	0.884[1]	28.35	....	....

[1] Amount of lactic acid less the amount of acid in the fresh milk.

for making an analysis at each stated period of time, no flask being opened until its contents were used. The results of these experiments are given in the table on preceding pages.

Decrease of Milk-sugar.

In all cases the loss of milk-sugar increased quite rapidly for thirty-two hours, after which additional change was slow and small. In seventy-two to one hundred and twenty hours the maximum loss was reached; in experiment No. 1 no further change of milk-sugar occurred after seventy-two hours, and in No. 2 none after ninety-six hours. Of course, at temperatures somewhat higher, less time would be required for the transformation of the same amount of milk-sugar. Averaging our results, we find that about 11 per cent of the sugar present in the milk at the start had disappeared in eight hours, 21 per cent in twenty-four hours, 25.5 per cent in thirty-two hours, 26 per cent in forty-eight hours, 27 per cent in seventy-two hours, and 27.6 per cent in ninety-six hours.

Amount of Lactic Acid Formed.

The maximum amount of lactic acid formed, calculated as lactic acid, was about 0.90 per cent, which is equivalent to about 62 per cent of the milk-sugar that disappeared. It is customary to represent in the following manner the reaction by which milk-sugar is converted into lactic acid:

$$C_{12}H_{22}O_{11} + H_2O = 4C_3H_6O_3.$$

According to this expression, all the milk-sugar is converted into lactic acid, weight for weight. While this equation expresses the most prominent chemical reaction that occurs, it certainly fails to give anything like a complete or accurate statement of the entire chemical reaction. In detail, our average results are as follows: In twenty-four hours, 40 per cent of the milk-sugar that had disappeared formed acid, largely lactic; in thirty-two hours, 58.5 per cent; in forty-eight hours, 64 per cent; in seventy-two hours, 63.3 per cent; in ninety-six hours, 63.5 per cent; in one hundred and twenty hours, 61.3 per cent.

As shown by Kayser,[1] there may be present in addition to lactic acid, as the products of the decomposition of milk-sugar by lactic-acid forming organisms, carbon dioxide gas, formic acid, acetic acid, acetone, and alcohol. Mayer[2] has found that under the most favorable conditions we may possibly be able to get as much as 83.9 parts of lactic acid from 100 parts of milk-sugar, but the conditions used by him are not such as normally exist in milk. The presence of alcohol, volatile fatty acids, and gases among the lactic-acid fermentation-products has also been shown by Leichmann,[3] and acetone by Jaksch.[4] The quantity of acid formed is, according to Emmerling,[5] dependent upon a variety of conditions, among which the following may be mentioned: The kind of organism; the reaction of the material, a neutral reaction being favorable; the presence or absence of air, the presence of air favoring the formation of more of the volatile acids; the conditions of nutrition, of temperature, and of the presence or absence of certain substances.

According to Timpe,[6] for example, one of the lactic acid organisms studied by him is checked in its growth by 0.04 per cent of free lactic acid. However, the growth is not checked so long as there are substances present with which the acid can unite. We have such substances in milk. Using as a basis the figures given by Söldner,[7] the inorganic compounds in 100 grams of milk would unite with 0.3938 gram of lactic acid. Timpe found that 100 grams of milk-casein neutralize 8.415 grams of lactic acid. The milk-casein in 100 grams of milk containing 2.5 per cent of casein would therefore neutralize 0.2104 gram of lactic acid. Thus, the total amount of lactic acid neutralized by 100 grams of ordinary milk would be 0.604 per cent, and this was about the amount of acid found by him in milk that had soured in the usual way. In his experience the maximum amount of acid is

[1] Ann. Past. **8**, 737 (1894).
[2] Centrbl. Bakt., **12**, 99 (1892).
[3] *Ibid.*, **16**, 826 (1894).
[4] Ber. d. chem. Ges., **19**, 781, R.
[5] Die Zersetzung stickstofffreier organischen Substanzen durch Bakterien, p. 34.
[6] Arch. Hyg., **18**, 1 (1893).
[7] Landw. Versuchs.-Stat., **38**, 351 (1889).

reached in about fifty hours at ordinary temperatures. Our results are somewhat higher than those of Timpe. We find as our maximum somewhat more lactic acid, which is nearly all formed in forty-eight to seventy-two hours. There will, of course, be a variation in different milks dependent upon the amount of casein and inorganic salts, other conditions being uniform. Richet[1] states that he has found as much as 1.6 per cent of lactic acid in sour milk, but this figure is so much higher than any one else has found that there must be some error in his method of determination. Hueppe[2] finds the amount of lactic acid formed in sour milk about 0.8 per cent, which is in close agreement with our results.

Relation of Coagulation of Milk to Amount of Acid.

In the case of experiment No. 3, the milk was found completely coagulated, that is, solidified in a mass, in twenty-six hours, when the amount of acid had reached about 0.6 per cent. In experiment No. 4, the time of coagulation was twenty-four hours and the percentage of acid was nearly 0.8. The milk in No. 2 had just coagulated at the end of twenty-four hours. In the case of experiments 1 and 4, the milk coagulated during the night and our observation was made in the morning, just how long after coagulation we do not know. Under the ordinary conditions of souring, we can expect, according to these results, that milk will coagulate when the total acid reaches about 0.8 or 0.9 per cent, as indicated by titration with standard alkali and phenolphthalein as indicator. Deducting the amount of the original titration of the fresh milk and calling the rest lactic acid, we have coagulation taking place when the lactic acid reaches 0.6 to 0.7 per cent. In producing this amount of lactic acid about 1.3 per cent of milk-sugar disappears, which is about 25 per cent of the sugar originally present in the milk.

Soluble Nitrogen Compounds in Sour Milk.

The soluble nitrogen compounds in the sour milk amounted to about 22 per cent of the nitrogen in the milk. This is

[1] Compt. rend., **86**, 550 (1878).
[2] Mittheil. a. d. Gesundh., **2**, 309 (1884).

practically all accounted for by the milk-albumin. The constancy of the amount of soluble nitrogen also suggests that it was present mostly, if not entirely, as milk-albumin.

Formation of Casein Monolactate and Casein Dilactate in Milk Coagulated by Ordinary Souring.

When the milk was first visibly coagulated the amount of casein in the form of monolactate was 13 to 14 per cent of the casein in the milk, and the amount of casein dilactate was 86 to 87 per cent of the casein in the milk. As the milk grew more acid, the monolactate gradually passed into the dilactate. The minute amount of monolactate apparently present at the time the experiment was stopped is due to a slight solubility of dilactate in a 5 per cent solution of sodium chloride. When milk coagulates by souring in the usual way, the casein is nearly all in the form of dilactate at the time the milk has set in a solid mass.

It was desired to determine the amount of casein monolactate in milk before the milk visibly coagulates. For studying this point, some milk was set aside one day at 5 P. M. and the next forenoon was warmed to about 40° C., when casein monolactate separated from the milk. In this case 65 per cent of the casein was in the form of monolactate, while no dilactate was present.

Separation of Casein, Casein Monolactate, and Casein Dilactate.

The method employed by us in separating casein, casein monolactate, and casein dilactate, when they occur together in milk, is as follows: The milk is heated to 40° C. and the monolactate separates as a precipitate. When only casein and casein monolactate are present, simple filtration with washing serves to separate them. When the two lactates are present in the coagulum formed after heating, they are removed from other milk constituents by filtration, and the monolactate is dissolved in a 5 per cent solution of sodium chloride at about 55° C., after which the two compounds are separated by filtration.

Summary.

1. The purpose of the work described in this paper was to study the chemical changes that take place in the ordinary souring of milk, especially those changes that affect the decomposition of milk-sugar, the formation of lactic acid, and the production of casein monolactate and casein dilactate.

2. The loss of milk-sugar increased quite rapidly for thirty-two hours at room temperatures (18° to 27° C.), after which the change was small and ceased in seventy-two to ninety-six hours, when the maximum loss of milk-sugar was reached, about 1.50 per cent, equivalent to about 28 per cent of the sugar originally present in the milk.

3. The maximum amount of lactic acid formed was about 0.9 per cent, which is equivalent to about 62 per cent of the milk-sugar that disappeared.

4. At the temperature used, the milk coagulated in twenty-four to twenty-nine and a half hours, when the percentage of total acid shown by titration had reached 0.6 to 0.7.

5. When the milk was first visibly coagulated, 13 to 14 per cent of the casein was in the form of monolactate and 86 to 87 per cent was in the form of dilactate. With further increase of acid in the milk, the monolactate passes into the dilactate.

GENEVA, N. Y., March 1, 1904.

Contributions from the New York Agricultural Experiment Station.

IX.—A STUDY OF THE ARTIFICIAL DIGESTION OF SOME COMPOUNDS OF CASEIN AND PARACASEIN CONTAINED IN COTTAGE AND CHEDDAR CHEESE.

BY LUCIUS L. VAN SLYKE AND EDWIN B. HART.

There is a popular belief, which appears to have some foundation in experience, that certain compounds of casein used as food are more digestible than certain compounds of paracasein also used as food. Put into the ordinary mode of expression, it is commonly believed that fresh cottage, or Dutch, cheese is more easily digested than cheddar cheese, especially new cheddar cheese. Cottage cheese, also com-

monly known as Dutch cheese, is prepared by allowing milk to coagulate by ordinary souring, heating to aid separation of whey, allowing the curd to drain, and then shaping it into balls. When thus prepared, it consists essentially of casein dilactate, holding 70 to 75 per cent of moisture. The coagulation is sometimes aided by adding a small amount of rennet, in which case the cheese is largely paracasein dilactate. Cottage cheese may also be prepared by adding 0.6 per cent of lactic acid or 0.25 per cent of hydrochloric acid to milk, forming in the latter casein dihydrochloride. In new cheddar cheese, the kind that is most commonly made and consumed in America, the nitrogen is largely in the form of paracasein monolactate.

It seemed desirable to ascertain by artificial peptic digestion to what extent laboratory experiments are in harmony with the popular belief referred to. We have worked with the following materials: Paracasein, paracasein monolactate of new cheddar cheese, paracasein dilactate, casein monolactate, casein dilactate (cottage cheese) prepared by normal souring of milk and by direct addition of lactic acid to milk, and casein dihydrochloride. These materials have been treated with varying amounts of pepsin, with and without hydrochloric acid. Some experiments were also made to determine the influence of the fineness of the materials upon the rate of digestion.

(*1*) *Comparison of Digestibility of Paracasein and Paracasein Monolactate without Acid.*

The paracasein used in this experiment was prepared by coagulating fresh milk with rennet extract; it was carefully washed. As the source of paracasein monolactate, we used freshly prepared cheddar cheese in which over 75 per cent of the nitrogen was present in the form of paracasein monolactate. The samples (25 grams) were ground with sand and in each of several bottles there was placed material equivalent to 0.694 gram of nitrogen with 80 cc. of water. The bottles and contents were heated to 100° C. for fifteen minutes to destroy all enzymes and active organisms. After cooling, there were

added to each bottle 3 cc. of chloroform and 20 cc. of pepsin solution containing 0.150 gram of Parke Davis & Co.'s aseptic scale pepsin. The bottles were kept at 37° C. and examined at intervals. Enough bottles were prepared in each case so that one bottle was used for each examination, no bottle being opened until analyzed. The analytical results are given in Table I.

These results show that the paracasein failed to digest, while the paracasein monolactate digested quite rapidly when we consider the absence of free acid.

(2) *Comparison of Digestibility of Casein Monolactate and Casein Dilactate without Acid.*

The casein monolactate was prepared by treating 20 pounds of milk with 32.6 grams of lactic acid. On heating at 37° to 40° C., the monolactate separated as a characteristic rubber-like mass. A portion of it was found, on testing, to dissolve completely in a 5 per cent solution of sodium chloride. The casein dilactate was prepared by allowing milk to sour in the usual way for making cottage cheese. These materials, carefully washed, were prepared for digestion as described under (1) preceding, except that in each bottle we used 0.200 gram of pepsin, in place of 0.150 gram, and 1 per cent of chloroform instead of 3 per cent. The amount of nitrogen in the material in each bottle was 0.830 gram. No acid was added to the contents of the bottles. The results are given in Table II.

The casein monolactate digested, in the absence of free acid, somewhat more rapidly than the dilactate. This result we did not anticipate, since it was expected that the compound containing the higher amount of acid would be acted upon more readily by pepsin. In explanation of this behavior, it may be suggested that the acid in the dilactate appears to be in more stable combination than in the monolactate.

(3) *Comparison of the Digestibility of Paracasein Monolactate and Paracasein Dilactate with and without Free Acid.*

The paracasein dilactate was prepared by allowing 20

Table I.—Showing Digestion of Paracasein and Paracasein Monolactate by Pepsin without Free Acid.

Material containing	Per cent of nitrogen in material.	Per cent of nitrogen in form of paracasein monolactate.	Per cent of nitrogen in material in soluble form.	Percentage of nitrogen in material expressed in form of water-soluble nitrogen.				
				In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
				Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Paracasein	4.11	....	2.43	6.62	6.62	7.06	7.64	6.62
Paracasein monolactate	3.52	75.27	3.98	17.00	22.62	22.91	40.78	45.96

Table II.—Showing Digestion of Casein Monolactate and Casein Dilactate by Pepsin without Acid.

Material.	Percentage of nitrogen in material.	Total nitrogen in each bottle.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
			In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
		Gram.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Casein dilactate	2.34	0.830	8.56	11.81	21.69	22.65	23.37
Casein monolactate	4.15	0.830	14.34	16.51	23.61	26.63	29.64

pounds of milk, mixed with half a pound of sour milk, to stand eight hours at room temperature and then adding 0.5 cc. of rennet extract, after which the mass was allowed to remain until it had become quite acid and was completely coagulated. The monolactate was obtained in the form of new cheddar cheese, in which 66.21 per cent of the nitrogen was in the form of monolactate. These materials were prepared for digestion as described under (1) preceding, except that we used 0.300 gram of pepsin and 1 cc. of chloroform, and in experiments 3 and 4 we used in addition 0.4 per cent of hydrochloric acid.

In studying the data embodied in Table III., we notice the same fact to which attention has already been called, *viz.*, that in the absence of free acid the monolactate undergoes pepsin digestion more rapidly than the dilactate. When, however, free acid is present, the reverse is true, the dilactate digesting more readily than the monolactate. The initial activity of digestion is considerably greater in both cases in the presence of acid. The following explanation is suggested to show why, in the presence of free acid, the dilactate digests more rapidly: The monolactate is first converted into dilactate and thus uses some of the acid, so that less acid is left free to take part in the pepsin digestion.

(4) *Comparison of Digestibility of Casein Dilactate and Casein Dihydrochloriae with and without Acid.*

The casein dilactate and casein dihydrochloride were prepared by treating milk with 0.6 per cent of lactic acid and 0.2 per cent of hydrochloric acid. The resulting products were washed and prepared for digestion as described in (1) and (3) preceding, except that the materials were not ground with sand and were not heated. In 1 and 2 no free acid was added to the digestion bottles, while in 3 and 4 we used 0.4 per cent of hydrochloric acid (see Table IV., p. 159).

The data in Table IV. show no essential difference in digestibility between the casein dilactate and casein dihydrochloride. This is true both in the absence and presence of free acid. Increased digestibility is caused by free acid, the

Table III.—Showing Digestion of Paracasein Monolactate and Dilactate with and without Acid.

	Material.	Per cent of hydrochloric acid used in digestion.	Total nitrogen in material in each bottle.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
				In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
			Gram.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Paracasein monolactate	0	0.710	23.66	27.46	49.72	51.84	62.11
2	" dilactate	0	"	14.23	14.51	24.37	31.83	33.52
3	" monolactate	0.4	"	48.31	56.63	46.77	51.56	57.33
4	" dilactate	0.4	"	67.75	73.35	70.43	67.89	73.39

Table IV.—Showing Digestion of Casein Dilactate and Casein Dihydrochloride with and without Acid.

	Material.	Per cent of hydrochloric acid used in digestion.	Total nitrogen in each bottle.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
				In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
			Gram.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Casein dilactate	0	0.730	11.37	17.95	34.25	42.47	49.05
2	" dihydrochloride	0	"	11.65	15.07	31.51	43.42	50.69
3	" dilactate	0.4	"	84.94	84.53	96.58	96.04	96.50
4	" dihydrochloride	0.4	"	83.56	85.90	92.20	94.94	97.27

most marked increase being in the first period (four hours) of digestion.

(5) *Comparison of Digestibility of Cottage Cheese Made from Whole Milk and Skim-milk.*

We desired to test the influence of fat in cottage cheese upon its digestibility. The cheese was prepared in each case by adding 0.2 per cent of hydrochloric acid to the milk used. We thus had casein dihydrochloride as our proteid, containing, in one case, 12.65 per cent of fat and, in the other, 0.62 per cent. The materials were prepared for digestion as described in (4) preceding.

The results in this table indicate that the cheese made from whole milk digested more quickly than the cheese made from skim-milk. This could not be accounted for by saying that the whole milk contained more proteolytic enzyme than the skim-milk, because milk-enzymes, even when present in different quantities, do not appear to have the power of producing such differences of digestion in so short a time. The true explanation probably lies in the fact that the whole-milk cheese was much more porous and loose in texture, owing to the presence of the fat, and so offered a better mechanical condition for the action of the digestive agent. The fat in this case not only failed to impede digestion but indirectly favored it.

(6) *Influence of Mechanical Division upon Digestion of Cheese.*

The mechanical condition or fineness of division of food is known to have a marked influence upon digestion. In testing this point, we prepared fresh cheddar cheese and fresh cottage cheese. The cheddar cheese contained 70.4 per cent of its nitrogen as paracasein monolactate. All the bottles contained the same content of water and 0.4 per cent of hydrochloric acid. In Experiment 1, the cottage cheese was made as fine as possible by grinding with quartz sand, while in 2 the cheese was in the condition in which it is ordinarily consumed. In Experiment 3, the cheddar cheese was ground with sand, in 4 it was chopped about as fine as it would be made

Table V.—Showing Digestion of Cottage Cheese Made from Whole Milk and Skim-milk.

Cheese made from	Per cent of fat in cheese.	Per cent of hydrochloric acid used in digestion.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
			In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Whole milk	12.65	0.4	80.97	87.02	88.23	93.26	93.95
Skim-milk	0.62	0.4	68.00	80.28	89.97	93.09	92.91

Table VI.—Showing Influence of Mechanical Division of Cheese upon Digestion.

	Material.	Total nitrogen in each bottle.	Per cent of hydrochloric acid used in digestion.	Percentage of nitrogen in material, expressed in form of water-soluble nitrogen.				
				In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
		Gram.		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Cottage cheese, ground fine	0.772	0.4	78.11	91.20	92.49	90.81	90.42
2	" " not ground	"	"	68.27	75.39	89.90	88.86	97.53
3	Cheddar cheese, ground fine	"	"	63.08	72.80	80.32	76.04	83.28
4	" " chopped fine	"	"	34.07	55.54	65.16	78.50	81.87
5	" " in $\frac{1}{4}$-in. cubes	"	"	18.27	29.92	50.78	64.52	69.17

by ordinary chewing, and in 5 it was cut into cubes about one-quarter of an inch in size. In other respects the materials were prepared for digestion as described in (4) preceding (see Table VI., p. 161).

The difference of digestion between the finely ground cottage cheese and that left in the ordinary condition is not large, and after twenty-four hours nearly disappears. In the case of the cheddar cheese, the difference is very striking. When the cheese was ground fine, about twice as much was digested in four hours as when it was chopped fine, and about three and one-half times as much as when cut into quarter-inch cubes. The cottage cheese in its ordinary condition digested more rapidly than the cheddar cheese ground fine.

(7) *Influence of Increasing Amounts of Acid upon Digestion of Cheese.*

In normal gastric digestion in animals, the acid used is secreted gradually and not all poured into the stomach at the start. In order that the conditions of our work might in this respect more nearly approximate normal digestion, we prepared for digestion, as described in (6) preceding, some samples of cottage and cheddar cheese, ground with sand, and added to the digesting mass hydrochloric acid at intervals, as follows: At the start, 0.4 per cent of acid; in two hours, 0.1 per cent; in four hours, 0.1 per cent; in eight hours, 0.1 per cent; in twenty-four hours, 0.1 per cent; in forty-eight hours, 0.1 per cent, making in all an addition of 0.9 per cent of hydrochloric acid. The results are given below in comparison with some digestions in which we used 0.4 per cent of acid at the beginning and added none afterwards.

The addition of 0.4 per cent of hydrochloric acid at the beginning of the digestion, followed by an addition of 0.1 per cent two hours after, increased the amount of digested proteid very noticeably at the first examination, four hours after the digestion began. This was true in both cottage and cheddar cheese. As in previous cases, the cottage cheese was more completely digested than the cheddar cheese.

Table VII.—Showing Effect of Increasing Amounts of Acid upon Digestion of Cheese.

	Material.	Total nitrogen in each bottle.	Per cent of hydrochloric acid used in digestion.		Percentage of nitrogen in material in form of water-soluble nitrogen.				
			Added at start.	Added at intervals.	In four hours.	In eight hours.	In twenty-four hours.	In forty-eight hours.	In seventy-two hours.
		Gram.			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Cottage cheese	0.772	0.4	..	78.11	91.20	92.49	90.81	90.42
2	" "	"	..	0.9	86.54	93.91	94.56	91.96	93.26
3	Cheddar "	"	0.4	..	63.08	72.80	80.32	76.04	83.28
4	" "	"	..	0.9	78.10	75.91	80.97	87.95	90.68

Summary.

1. In the absence of acid, paracasein fails to be digested by pepsin, while paracasein monolactate (the chief nitrogen compound of fresh cheddar cheese), paracasein dilactate, casein monolactate, casein dilactate (cottage or Dutch cheese), and casein dihydrochloride are partially digested. Paracasein monolactate and casein monolactate, in the absence of acid, are digested more than are paracasein dilactate and casein dilactate.

2. In the presence of 0.4 per cent of hydrochloric acid, paracasein dilactate is digested by pepsin more than is paracasein monolactate. Paracasein monolactate and dilactate, and casein monolactate and dilactate, and casein dihydrochloride digest more readily and completely in the presence of free hydrochloric acid than in its absence.

3. Casein dilactate and casein dihydrochloride do not differ in the rapidity and extent to which they are converted into soluble compounds by pepsin.

4. The addition of acid after the beginning of the digestion increases the amount of proteid digested in both cottage and cheddar cheese.

5. Cottage cheese made from whole milk digests more rapidly than that made from skim-milk, owing to the looser texture of the former. Fat in such cases does not impede digestion.

6. The rapidity of digestion is dependent in part upon the fineness of division of the material to be digested. Cottage cheese, as ordinarily consumed, is in a state of finer division than cheddar cheese.

7. Cottage cheese may properly be regarded as more readily digestible than new cheddar cheese for two reasons: First, the casein dilactate, the chief solid constituent of cottage cheese, is more digestible in the presence of free hydrochloric acid than is paracasein monolactate, the principal nitrogenous constituent of new cheddar cheese. Second, cottage cheese is in such a mechanical condition that it admits of easier attack by digestive agents than does new cheddar cheese.

GENEVA, N. Y., March 1, 1904.

Contributions from the Chemical Laboratory of Lehigh University.

VI.—PROPANETRISULPHONIC ACID.

[PRELIMINARY PAPER.]

By William B. Schober.

The only derivatives of propanetrisulphonic acid heretofore described are two barium salts prepared by Schaüfelin[1] in 1868. He treated trichlorhydrine (made by treating dichlorhydrine with phosphorus pentachloride) with a concentrated water solution of neutral potassium sulphite. The reaction, taking place in accordance with the following equation, was complete in twelve hours:

$$C_3H_5Cl_3 + 3K_2SO_3 = C_3H_5(SO_3K)_3 + 3KCl.$$

Owing to the formation of a double salt it was impossible to obtain the potassium propanetrisulphonate free from potassium chloride. He, therefore, treated a solution of the double salt with concentrated sulphuric acid and evaporated it on a water-bath until the odor of hydrochloric acid was no longer perceptible. The residue was extracted with alcohol, boiled with water, and neutralized with barium carbonate. After filtering the hot solution and cooling, a difficultly soluble, white, crystalline powder was deposited. It contained no water of crystallization. A determination for barium and sulphur gave these results:

	Calculated for $C_3H_5(SO_3)_3ba$.	Found.
Ba	42.2	42.04
S	19.8	20.2

By diluting the solution he obtained another barium salt, easily soluble, containing water of crystallization. After drying the salt at 150°, a determination for barium gave 41.8 per cent. No other results are recorded.

In order to avoid the difficulty encountered by Schaüfelin, I treated 1,2,3-tribrompropane (tribromhydrine) with ammonium sulphite. The tribromhydrine was prepared by treat-

[1] Ann. Chem. (Liebig), 148, 117.

ing allyl iodide with bromine. After being purified it boiled at 216° (uncorr.).

The ammonium sulphite was made by passing cooled sulphur dioxide, from copper and sulphuric acid, and cooled ammonia, obtained by gently heating concentrated ammonium hydroxide, into 95 per cent alcohol surrounded by a freezing-mixture of ice and salt. I obtained more satisfactory results by employing 95 per cent alcohol than with the absolute. When the latter was used the product was very finely divided and exceedingly difficult to filter.

The tribromhydrine and a saturated solution of 5 molecules of ammonium sulphite were placed in a flask, to which was attached an inverted condenser, and heated on a sand-bath. The substances reacted very slowly. At times, during the progress of the reaction, sulphur dioxide escaped; in order to avoid this a little ammonium carbonate was added. The heating was continued until all the tribromhydrine had disappeared. The hot, clear solution was filtered and allowed to stand over night. No crystals were deposited. Upon evaporation and cooling, a quantity of ammonium bromide separated out. On further treatment small quantities of ammonium sulphate and more ammonium bromide were obtained. Finally the crystals of what proved to be the ammonium salt of propanetrisulphonic acid were deposited.

The Ammonium Salt, $C_3H_5(SO_3NH_4)_3 + H_2O$.—This salt is very soluble in water with marked lowering of the temperature, difficultly soluble in absolute alcohol, from which it crystallizes in a fine powder composed of minute needles. It has a strong crystallizing force. From a water solution beautiful, brilliant, transparent crystals may be easily obtained. In one experiment a single crystal weighing 12 grams was formed. The salt is efflorescent on long standing; does not melt or char at 360°. A partial analysis gave these results:

I. 0.3419 gram substance, on heating for two hours at 130°, lost 0.0178 gram.

II. 0.1866 gram substance, on heating for one hour at 130°, lost 0.0098 gram.

III. 0.1768 gram substance gave 0.02336 gram N (Kjeldahl-Gunning method).

IV. 0.1454 gram substance, dried at 125°, gave 0.3027 gram $BaSO_4$ (Carius method).

V. 0.1465 gram substance, dried at 125°, gave 0.3058 gram $BaSO_4$ (Carius method).

	Calculated for $C_3H_5(SO_3NH_4)_3 + H_2O$.	Found. I.	II.
H_2O	5.10	5.20	5.25
N	12.53	....	13.2
S	28.62	28.58	28.65

The Barium Salt, $(C_3H_5(SO_3)_3)_2Ba_3 + 5H_2O$.—This salt was made by dissolving the ammonium salt in water and boiling the solution with barium carbonate until the odor of ammonia was no longer perceptible. It is difficultly soluble in hot alcohol, difficultly soluble in water, from which it crystallizes in minute, ill-defined crystals. An analysis gave the following results:

I. 0.3064 gram substance lost 0.0269 gram on heating for two hours at 125°, and gave 0.2001 gram $BaSO_4$.

II. 0.5256 gram substance lost 0.0464 gram on heating one and a half hours at 125°, and gave 0.3448 gram $BaSO_4$.

III. 0.2387 gram substance, dried at 130°, gave 0.0726 gram CO_2 and 0.0366 gram H_2O.

IV. 0.1997 gram substance, dried at 130°, gave 0.0586 gram CO_2 and 0.0284 gram H_2O.

	Calculated for $C_3H_5(SO_3Ba)_3 + 5H_2O$.	Found. I.	II.
C	7.40	8.25	8.00
H	1.03	1.70	1.58
H_2O	8.47	8.82	....
Ba	42.24	42.34	....

The investigation of propanetrisulphonic acid and its derivatives will be continued.

SOUTH BETHLEHEM, PA.,
March 12, 1904.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF TRICHLORTRINITROBENZOL.

By C. Loring Jackson and Paul Shortt Smith.

In continuing an extended research, which has been carried on for some years in this laboratory, on the behavior of nitrohalogen derivatives of benzol, it was important to study the trichlortrinitrobenzol discovered by Wing and one of us[1] many years ago. At that time the substance was prepared without difficulty, but more than one man, who had taken up the work later in this laboratory, found it impossible to obtain any of it, although the directions given in the paper cited were followed with the greatest care. It was evident that some condition essential to the preparation of the trichlortrinitrobenzol had been omitted, but even consultation with Dr. Wing failed to show what this condition was. At last, however, Mr. H. A. Carlton discovered that it was necessary to use a return-condenser in converting the trichlordinitrobenzol into trichlortrinitrobenzol, and with this slight change the preparation became once more the easy one described by Wing and one of us. As Mr. Carlton had become interested in another part of the work during his experiments on the manufacture of trichlortrinitrobenzol, we have undertaken the study of this substance.

An alcoholic solution of sodic ethylate reacted vigorously with the trichlortrinitrobenzol, forming even at ordinary temperatures trinitrophloroglucine triethyl ether and trinitrophloroglucine, $C_6(OH)_3(NO_2)_3$. This action therefore resembles in part the behavior of the tribromtrinitrobenzol,[2] which under these conditions gives the same products, but also by a parallel reaction a considerable quantity of tribromnitroresorcine diethyl ether, $C_6Br_3NO_3(OC_2H_5)_2$. No trace of a corresponding replacement of nitro groups was observed by us with the chlorine compound. Trichlordinitrobenzol[3] in the cold formed chlordinitroresorcine diethyl ether, which gives

[1] This Journal, 9, 354 (1887).

[2] Jackson and Warren: *Ibid.*, 15, 607 (1893).

[3] Jackson and Lamar: *Ibid.*, 18, 664 (1896).

dinitrophloroglucine triethyl ether with a hot solution of sodic ethylate; and the tribromdinitrobenzol[1] gives two bromdinitroresorcine diethyl ethers and dinitrophloroglucine triethyl ether as the principal products in the cold, while, when hot sodic ethylate is used, one of the bromdinitroresorcine diethyl ethers is reduced to dinitroresorcine diethyl ether.

With sodic malonic ester one of the atoms of chlorine in the trichlortrinitrobenzol is replaced by the malonic ester radical, but instead of the expected malonic ester the substance isolated by us was a dichlortrinitrophenylacetic ester,

$$C_6Cl_2(NO_2)_3CH_2COOC_2H_5,$$

melting at 130° to 131°, formed by the decomposition of the malonic ester. It is probable that the acetic ester was formed during the distillation with steam used by us in purifying the product, but our attempts to prove this by isolating a pure compound without distillation with steam led to no result. Parallel experiments by H. A. Carlton and one of us[2] with tetrachlordinitrobenzol, however, showed that the trichlordinitrophenylmalonic ester was obtained, when the substance was purified by solution only, whereas the acetic ester was obtained when the mother-liquors were distilled with steam. This, although not conclusive, is strongly in favor of our theory that the acetic ester is formed by the distillation with steam. Tribromtrinitrobenzol,[3] when treated with sodic malonic ester, gives bromnitrophenylmalonic ester,

$$C_6HBr(NO_2)_3CH(COOC_2H_5)_2,$$

by the replacement of 1 atom of bromine by the malonic ester radical, and of a second by hydrogen. No similar replacement of chlorine by hydrogen was observed in our work nor has one ever been observed so far as we can find. The tribromdinitrobenzol[4] and the trichlordinitrobenzol[5] show the same difference in their behavior toward sodic malonic ester as that which appears with the trinitro compounds.

[1] Jackson and Koch: This JOURNAL, **21**, 510.
[2] *Ibid.*, **31**, 360 (1904).
[3] Jackson and Moore: *Ibid.*, **12**, 7 (1890).
[4] Jackson and Robinson: *Ibid.*, **11**, 93, 541 (1889).
[5] Jackson and Lamar: *Ibid.*, **18**, 664 (1896).

In our attempts to obtain a substitution of chlorine by hydrogen we treated the dichlortrinitrophenylacetic ester with sodic malonic ester, and obtained the replacement of a second atom of chlorine by the malonic ester radical, but our analysis of the substance was not sufficient to determine whether it was the chlortrinitrophenyleneaceticmalonic ester,

$$C_6Cl(NO_2)_3CH_2COOC_2H_5CH(COOC_2H_5)_2,$$

or the chlortrinitrophenylenediacetic ester,

$$C_6Cl(NO_2)_3(CH_2COOC_2H_5)_2.$$

The latter would be the more probable, as the product was worked up by distillation with steam, but, as the analysis on the whole agrees better with the first formula, we have adopted that provisionally for this substance, which melts at 147° to 148°. Unfortunately the insufficiency of our analysis was discovered only after the departure of one of us from Cambridge prevented us from furnishing better analytical data. The bromtrinitrophenylmalonic ester[1] is also converted into trinitrophenylenedimalonic ester by the further action of malonic ester.

Further treatment with sodic malonic ester removed chlorine as sodic chloride from the chlortrinitrophenyleneaceticmalonic ester, but the organic product was so unmanageable that we can give no account of its nature.

The dichlortrinitrophenylacetic ester was converted by treatment with aniline into dianilinotrinitrophenylacetic ester,

$$C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5,$$

melting at 201°, which forms a compound with benzol,

$$C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5.2C_6H_6.$$

This result, taken in conjunction with those of Herman and one of us[2] on trianilinodinitrobenzol, and Carlton and one of us[3] on trianilinochlordinitrobenzol, indicates that the tendency to form addition-compounds is a marked one among nitroani-

[1] Jackson and Moore: This JOURNAL, 12, 7 (1890).
[2] *Ibid.*, 16, 35 (1894).
[3] *Ibid.*, 31, 360 (1904).

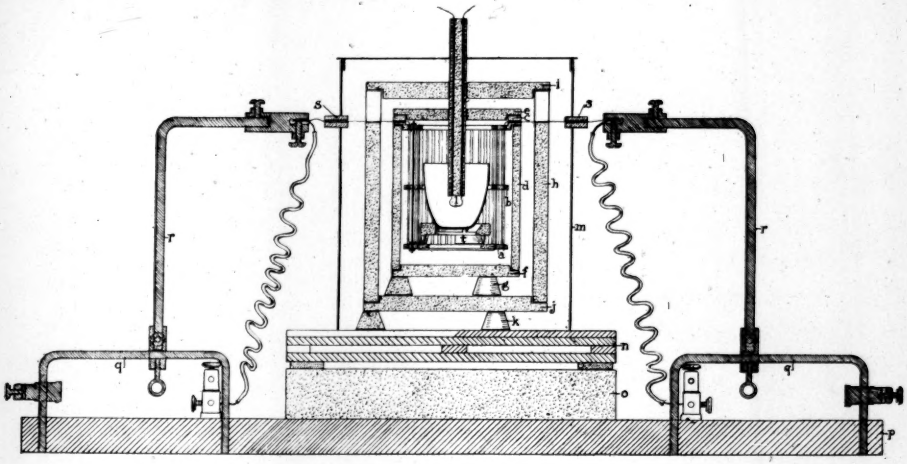


Fig. IV.

linobenzols. This subject will be studied more fully in this laboratory.

When heated to 150° to 160° in a sealed tube with strong hydrochloric acid the dichlortrinitrophenylacetic ester was converted into a new 3,5-dichlor-2,4,6-trinitrotoluol, melting at 200° to 201°, by the saponification of the ester, followed by the removal of carbonic dioxide. Under the same conditions the chlortrinitrophenylenemalonicacetic ester gave a substance which, although not fully purified, was evidently the chlortrinitroxylol of Klages and Knoevenagel.[1]

The constitution of all the new compounds mentioned in this paper follows from the fact that they are prepared from the symmetrical 1,3,5-trichlor-2,4,6-trinitrobenzol.

EXPERIMENTAL PART.

Preparation of Trichlortrinitrobenzol.

The trichloraniline was prepared by the method of Victor Meyer and Sudborough,[2] that is, by passing chlorine through aniline dissolved in chloroform. The progress of the reaction was traced by filtering out a small quantity of the precipitate, washing it, and testing the aqueous washings with sodic hydrate; the amount of the precipitate of aniline formed showed the extent of the chlorination. The trichloraniline was converted into trichlorbenzol by the action of alcohol sulphuric acid and sodic nitrite by the method of Lamar and one of us.[3] In that paper it is stated that the trichlorbenzol was converted into trichlordinitrobenzol by standing with fuming nitric acid of sp. gr. 1.505 in the cold. With commercial acid of sp. gr. 1.5 we obtained only the mononitro compound. Accordingly, we heated the trichlorbenzol on the steam-bath for several hours with a mixture of three parts of fuming nitric acid of sp. gr. 1.5 and one of fuming sulphuric acid of sp. gr. 1.89. The mixture, on standing over night, deposited nearly pure trichlordinitrobenzol. The small amount remaining in the

[1] Ber. d. chem. Ges., **28**, 2046 (1895).

[2] *Ibid.*, **27**, 3151 (1894); compare also Jackson and Lamar: This JOURNAL, **18**, 666 (1896).

[3] This JOURNAL, **18**, 667 (1896).

acid mother-liquor was precipitated with water and purified by crystallization from alcohol.

The trichlortrinitrobenzol was prepared by the method recently rediscovered by Mr. H. A. Carlton in this laboratory. We have found the following arrangement of the process gives the best yield. Sixteen grams of trichlordinitrobenzol were mixed with 400 cc. of fuming nitric acid of sp. gr. 1.50 and 160 cc. of fuming sulphuric acid of sp. gr. 1.89. The nitric acid was a nearly colorless commercial fuming acid. An acid strongly colored with nitrous fumes would probably fail to give the desired result judging from previous experience.[1] The sulphuric acid was prepared by mixing sulphuric trioxide with strong sulphuric acid. The mixture was boiled in a flask with the inner tube of a return-condenser ground into the neck (this condition is indispensable to success) for two days, the boiling being carried on violently the whole time. On standing over night a considerable quantity of the trichlortrinitrobenzol crystallized out in small, white needles, which were filtered out through glass wool. The filtrate was precipitated with water and the precipitate recrystallized from alcohol. When 16 grams of trichlordinitrobenzol were used, 7 to 8 grams of trichlortrinitrobenzol usually crystallized from the acid, and about 2 grams were obtained from the filtrate by precipitation.

In our last series of preparations the following yields were obtained from 100 grams of aniline:

Trichloraniline, an essentially quantitative yield.
Trichlorbenzol, 95 grams.
Trichlordinitrobenzol, 100 grams.
Trichlortrinitrobenzol, 48 grams.

The yield of trichloraniline is decidedly better than that obtained by Lamar and one of us,[2] but the yield of trichlorbenzol was only little over half of that formerly obtained.

Action of Sodic Ethylate on Trichlortrinitrobenzol.

One gram of trichlortrinitrobenzol was dissolved in 4 cc. of

[1] Jackson and Wing: This JOURNAL, 9, 348 (1887).
[2] *Ibid.*, 18, 667 (1896).

benzol and mixed with the sodic ethylate made from 0.6 gram of sodium and 15 cc. of absolute alcohol, so that there was a large excess of sodic ethylate. The solution turned bright scarlet on the addition of the first drops of the sodic ethylate, and there was a considerable evolution of heat. The mixture was allowed to stand an hour at ordinary temperatures, after which it was acidified with dilute sulphuric acid, which removed the red color, filtered from the precipitated salts, and evaporated on the steam-bath till the solvents had been driven off. The slightly oily, crystalline residue was recrystallized from alcohol until it showed a constant melting-point. As this lay at 119°, and the substance gave no test for chlorine, it was evidently the trinitrophloroglucine triethyl ether.[1] For greater certainty it was dried *in vacuo* and analyzed.

0.2042 gram substance gave 23.1 cc. moist N_2 at 23° and 762 mm.

	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found.
N	12.17	12.78

The alcoholic mother-liquors from the trinitrophloroglucine triethyl ether contained a dark-green oil, from which we did not succeed in isolating any definite compound.

The precipitate obtained as one of the products of the reaction was in some cases filtered out before acidification. Upon washing with water most of it dissolved, and the solution after acidification with dilute sulphuric acid was concentrated and allowed to stand over night, when it deposited thick, yellowish-white needles, and, on further spontaneous evaporation, small, yellow, hexagonal prisms. The quantity was too small for complete purification, but both sorts of crystals melted from 160° to 165°. These observations show that the substance is the trinitrophloroglucine, $C_6(OH)_3(NO_2)_3.H_2O$, which melts with its water of crystallization at 160° to 161°, according to Warren and one of us,[2] at 158° according to Benedikt, but after being dried at 105° shows the melting-point 167°;[3] it also crystallizes in the two forms described.

[1] Jackson and Warren: This JOURNAL, 15, 611 (1893).
[2] *Ibid.*, 15, 615 (1893).
[3] Ber. d. chem. Ges., 11, 1376 (1878).

The behavior of trichlortrinitrobenzol with sodic ethylate therefore resembles that of tribromtrinitrobenzol with the same reagent so far as the replacement of halogen is concerned, but we observed no signs of the parallel reaction by which nitro groups are replaced in the tribromtrinitrobenzol.

Action of Sodic Malonic Ester on Trichlortrinitrobenzol.

Ten grams of trichlortrinitrobenzol were dissolved in 40 cc. of anhydrous benzol and mixed with the sodic malonic ester made by the action of 14 cc. of malonic ester and 2 grams of sodium previously treated with 40 cc. of absolute alcohol, that is, about 3 molecules of the malonic ester were used to each molecule of the trichlortrinitrobenzol. On the addition of the sodic malonic ester the mixture turned deep red, a precipitate was deposited, and there was a considerable evolution of heat. It was allowed to stand at ordinary temperatures in a corked flask for twenty-four hours, after which it was shaken with water in a separating-funnel, the oily layer acidified with dilute sulphuric acid, and washed with water. As the viscous residue obtained after the evaporation of the benzol showed no tendency to crystallize even after standing several days, the benzol solution was distilled with steam to remove the excess of malonic ester and perhaps other oily impurities. For this purpose the benzol solution was boiled with water in an evaporating-dish for fifteen to twenty minutes with constant stirring. On cooling, the organic substance solidified, and was found to be almost pure. Crystallization from alcohol raised it without difficulty to the constant melting-point, 130° to 131°, when it was dried *in vacuo* and analyzed. It is possible that a better solvent than alcohol could be found for this substance, if it were to be prepared in quantity, as alcohol brings about a decomposition of the compound when boiled for some time with it, shown by a darkening of the color and a lowering of the melting-point by about 2°. This prevents the easy isolation of additional pure material from the alcoholic mother-liquors.

I. 0.2455 gram substance gave, on combustion, 0.2960 gram CO_2 and 0.0573 gram H_2O.

II. 0.2222 gram substance gave 0.2632 gram CO_2 and 0.0432 gram H_2O.

III. 0.1792 gram substance gave, by the Carius method, 0.1391 gram AgCl.

IV. 0.1816 gram substance gave 0.1415 gram AgCl.

V. 0.2126 gram substance gave 0.1614 gram AgCl.

VI. 0.1574 gram substance gave 0.1237 gram AgCl.

	Calculated for $C_6Cl_3(NO_2)_3CH_2COOC_2H_5$.	Found. I.	II.	III.	IV.	V.	VI.
C	32.60	32.87	32.30	....	....	....	....
H	1.90	2.61	2.18	....	....	....	....
Cl	19.30	....	....	19.19	19.26	18.77	19.43

The substance is therefore the dichlortrinitrophenylacetic ester instead of the expected malonic ester. We were unable to determine whether the acetic ester was the direct product of the reaction or formed from the substituted malonic ester during the boiling with water, as all our attempts failed to isolate the product of the reaction without boiling it with water. The results of the work of Carlton and one of us[1] with trichlordinitrophenylmalonic ester indicate that the acetic ester is formed during distillation with steam, but they are not conclusive.

Properties of Dichlortrinitrophenylacetic Ester, $C_6Cl_3(NO_2)_3CH_2COOC_2H_5$.—It crystallizes in long, slender, white prisms, usually terminated by a single plane at an oblique angle, which are arranged in radiated groups. It melts at 130° to 131°, and is freely soluble in benzol, chloroform, or acetone; soluble in cold ethyl or methyl alcohol, ether, carbonic disulphide, or glacial acetic acid, more soluble in each of these solvents when hot; slightly soluble in ligroin; insoluble in water. The three strong acids have no action on it in the cold, and hydrochloric acid does not attack it when hot (except by long-continued heating). Hot, strong nitric acid gives a yellow solution with it; hot sulphuric acid a brown solution. A hot, aqueous solution of sodic hydrate gives a red solution with it, which undoubtedly contains its sodium salt.

[1] This JOURNAL, 31, 360 (1904).

Dianilinotrinitrophenylacetic Ester, $C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5$.—One gram of the dichlortrinitrophenylacetic ester was treated with an excess of aniline. The first drops of the aniline gave a bright red color at once, but on acidification and washing only a very slight precipitate could be obtained from the wash-waters with argentic nitrate. It seems possible, therefore, that this red color is due to the aniline salt of the phenylacetic ester. The mixture of aniline and the substance was accordingly heated on the steam-bath for two hours, at the end of which time it had solidified. After washing out the excess of aniline with dilute hydrochloric acid and water it was purified by crystallization from benzol, when it was found that it combined with 2 molecules of benzol to form yellow crystals, but if the crystallization took place under ordinary conditions, in addition to these yellow crystals small red needles, free from benzol, were deposited. In order to obtain only the compound containing benzol, we proceeded as follows: Some of the substance was dissolved in benzol with the aid of heat—it dissolves with difficulty in the cold—and the solution cooled by immersing the beaker in snow. The benzol was then evaporated off by passing a current of air over its surface, and in this way the yellow crystals, without a trace of the red, were obtained. They were dried on a porous plate, washed with a little cold benzol, and dried for analysis by exposure to the air in a cold place.

1.4451 grams substance lost, at 100°, 0.3829 gram.

	Calculated for $C_6(C_6H_5NH)_2(NO_2)_3CH_2COOC_2H_5.2C_6H_6$.	Found.
C_6H_6	24.53	26.50

This result is much further from the theoretical number than we could wish, but it lies still further from the percentage calculated for a compound with 3 molecules of benzol (32.77), and, as it represents an additional loss of only about 10 milligrams, an amount of benzol or moisture which might easily have been present considering the imperfect method of drying necessary on account of its instability, we think there can be no doubt that the formula given is correct. That the sub-

stance lost was benzol was proved by heating a sample in a test-tube, when a vapor was obtained recognized as benzol by its smell and method of burning.

Properties of the Benzol Addition-Compound of Dianilinotrinitrophenylacetic Ester.—It forms beautiful, golden-yellow crystals, which lose the benzol between 20° and 30° in a few hours, more rapidly at 100°. Owing to the ease with which the benzol is given off, this substance melts at the same temperature as the dianilinotrinitrophenylacetic ester, 201°.

The mixture of yellow and red crystals obtained in making dianilinotrinitrophenylacetic ester was crystallized from benzol until it showed the constant melting-point 201°, when it was dried at 100° and analyzed with the following result:

0.2527 gram substance gave 0.5146 gram CO_2 and 0.1067 gram H_2O.

	Calculated for $C_6(C_6H_5NH)_2(NO_2)_3CH_3COOC_6H_5$.	Found.
C	54.89	55.54
H	3.95	4.73

The result obtained is perhaps as near as could be expected, since the body decomposes explosively a few degrees above its melting-point. To meet this difficulty the substance was thoroughly mixed with fine cupric oxide in a copper boat about 15 cm. long, and the heat was applied with great caution. The analysis leaves no doubt as to the formula of the compound.

Properties of Dianilinotrinitrophenylacetic Ester, $C_6(C_6H_5NH)_2(NO_2)_3CH_3COOC_2H_5$.—It crystallizes from benzol at ordinary temperatures in long, slender, red prisms, terminated by a single plane at an oblique angle, but these prisms are usually mixed with yellow crystals of the benzol compound. It melts at 201°, and is freely soluble in acetone; soluble in chloroform when cold, freely soluble when hot; slightly soluble in cold benzol, freely in hot; slightly soluble in cold ether, carbonic disulphide, or glacial acetic acid, soluble in each of these solvents when hot; essentially insoluble in cold ligroin or methyl alcohol, soluble when hot; essentially insoluble in ethyl alcohol, slightly soluble in it when

hot; insoluble in water. Strong hydrochloric acid has no action on it; strong nitric acid has no action in the cold, but gives a yellow solution if hot; strong sulphuric acid gives a wine-colored solution in the cold, and chars it when hot. Sodic hydrate gives a yellow solution when hot.

Saponification of Dichlortrinitrophenylacetic Ester.

As our preliminary experiments on the action of sulphuric acid of sp. gr. 1.44 led to unsatisfactory results, we used strong hydrochloric acid as the saponifying agent. Five-tenths gram of the dichlortrinitrophenylacetic ester were heated with 4 cc. of strong hydrochloric acid in a sealed tube to 150° to 160° over night. The yellowish-white crystalline product was purified by crystallization from a mixture of three parts of alcohol with one of water, until it showed the constant melting-point 200° to 201°, when it was dried at 100°, and analyzed with the following result:

I. 0.1442 gram substance gave, by the Carius method, 0.1382 gram AgCl.

II. 0.2060 gram substance gave 0.1986 gram AgCl.

	Calculated for $C_6Cl_2(NO_2)_3CH_3$.	Found. I.	II.
Cl	23.99	23.69	23.84

The substance is therefore the dichlortrinitrotoluol,

$$Cl_3 3,5.(NO_2)_3 2,4,6,$$

and we cannot find that it has been described as yet. Two grams of the dichlortrinitrophenylacetic ester gave 1.4 grams of the dichlortrinitrotoluol, that is, 87 per cent of the theoretical yield.

Properties of the 3,5-Dichlor-2,4,6-trinitrotoluol, $C_6Cl_2(NO_2)_3CH_3$.—It crystallizes from dilute alcohol in white, long, slender, flat prisms, terminated by one plane at a sharp angle; less commonly in little crystals looking like elongated rhombohedra, probably the same form as the first but not flattened. It melts at 200° to 201°, and is freely soluble in benzol or acetone; soluble in cold chloroform, freely soluble in it when hot; slightly soluble in cold alcohol, freely in hot;

slightly soluble in methyl alcohol, ether, ligroin, carbonic disulphide, or glacial acetic acid when cold, soluble in each of these solvents when hot; insoluble in water. The best solvent for it is a mixture of three parts of alcohol with one of water. It is not affected by the three strong acids, or sodic hydrate even when hot.

Chlortrinitrophenyleneaceticmalonic Ester, $C_6Cl(NO_2)_3CH_2COOC_2H_5CH(COOC_2H_5)_2$.—Five grams of dichlortrinitrophenylacetic ester were dissolved in as little benzol as possible and mixed with the sodic malonic ester made from 5.2 cc. of malonic ester and 0.75 gram of sodium previously treated with 30 cc. of absolute alcohol, that is, 2 molecules of sodic malonic ester to 1 of the phenylacetic ester. On the addition of the sodic malonic ester the solution turned dark-claret, but there was no perceptible evolution of heat. The mixture was allowed to stand over night in a corked flask at ordinary temperatures when it was found that it had taken on a scarlet color. It was worked up by precipitation with water, acidifying the benzol solution with dilute sulphuric acid, washing again, and boiling for fifteen or twenty minutes with water in an evaporating dish with constant stirring. The product solidified on cooling, and was purified by crystallization from alcohol until it showed the constant melting-point 147° to 148°, when it was dried *in vacuo* and analyzed with the following results:

0.2569 gram substance gave, on combustion, 0.3867 gram CO_2 and 0.0809 gram H_2O.

	Found.
C	41.06
H	3.50

This analysis is not sufficient to establish the composition of the substance with certainty, and, as its insufficiency was not recognized before the departure of one of us from Cambridge, we are unable to add the necessary analytical data, but, although the nature of the body cannot be stated with certainty, our results lead to a very probable formula for it which we have adopted provisionally. The two probable formulas for it are,

I. $C_6Cl(NO_2)_3CH_2COOC_2H_5CH(COOC_2H_5)_2$,

formed by the replacement of a second atom of chlorine by the malonic ester radical, and,

II. $C_6Cl(NO_2)_3(CH_2COOC_2H_5)_2$,

formed from I. by saponification, followed by the removal of carbonic dioxide. The following table gives a comparison of the percentages of carbon and hydrogen in Formulas I. and II. with those found in our analysis:

	I.	Found.	II.
C	41.54	41.06	40.05
H	3.67	3.50	3.34

Our analytical results agree better with Formula I. than with II., but the percentage of water is actually smaller than that contained in Formula I., where it would be expected to be decidedly higher in a substance like this containing chlorine. On the other hand, the percentage of carbon found is a whole per cent above that contained in Formula II., and, if this were due to chlorine, which had escaped absorption, the hydrogen found must have come more than 0.16 per cent too high. It seems to us, therefore, that the more probable formula is I., and that the body may be called provisionally the chlortrinitrophenyleneaceticmalonic ester.

The yield was 2.4 grams of the new substance from 5 grams of dichlortrinitrophenylacetic ester, that is, 35 per cent of the theoretical yield.

Properties of the Chlortrinitrophenyleneaceticmalonic Ester, $C_6Cl(NO_2)_3CH_2COOC_2H_5CH(COOC_2H_5)_2$.—It crystallizes from alcohol in white, much-branched needles, at first arranged in round, radiating groups, which develop later into forms like birch rods. It melts at 147° to 148°, and is freely soluble in benzol, chloroform, or acetone; soluble in cold ether or carbonic disulphide, freely soluble in them when hot; soluble in cold ligroin, more soluble in hot, but not freely so; slightly soluble in ethyl or methyl alcohol or glacial acetic acid when cold, soluble when hot; insoluble in water. The best solvent for it is alcohol. The three strong acids have no action

on it in the cold, and hot hydrochloric acid does not affect it; hot nitric acid forms a red solution with it; hot sulphuric acid chars it. A hot aqueous solution of sodic hydrate gives a deep red solution with it—undoubtedly the sodium salt.

Attempts to saponify this substance in the usual way with sulphuric acid led to unsatisfactory results. With strong hydrochloric acid, at 160° to 170°, in a sealed tube, a well-crystallized body was obtained, but we did not have time to prepare enough of it for complete purification. As it melted in an impure state between 215° and 220°, there can be little doubt that it was the expected 5-chlor-2,4,6-trinitroxylol, which melts, according to Klages and Knoevenagel,[1] at 218°.

Upon treating the so-called chlortrinitrophenyleneaceticmalonic ester with sodic malonic ester, sodic chloride was formed, but no definite organic compound could be isolated from the sticky black product.

REVIEWS.

QUANTITATIVE CHEMICAL ANALYSIS. By DR. C. REMIGIUS FRESENIUS, Director of the Chemical Laboratory at Wiesbaden. Authorized translation of the Sixth German Edition, by ALFRED I. COHN, PH.G. New York: John Wiley & Sons. 1904. 8vo. 2 Vols. pp. xxxiv + 2035. Cloth, $12.50.

There is surely no occasion here to make any special reference to the many and peculiar excellencies of the last German edition of this work, hence the reviewer will mainly confine his remarks to points in which this translation appears to differ from the sixth German edition.

In accordance with the views of the author of this important treatise on Quantitative Analysis, the translator presents a judicious transformation of the out-of-date terminology to forms according with more modern views, still retaining the binary expression of the composition of salts; what is otherwise so well done is marred by the statement of the composition of potassium nitrate as KO and NO_5, and similarly of sodium nitrate, a view distinctly not harmonious with the rest of the book.

This translation exhibits less of German idiom than does the recent English edition of this work, and it has ge erally omitted nothing of the original text. Leading the typ gives a decided improvement in the appearance of the pages over

[1] Ber. d. chem. Ges., **28**, 2046 (1895).

that of the English edition, but this change alone adds over a third to the bulk and the cost of the book. Surely it would have improved the work to have left out the detail of such preparations as that of potassium permanganate and of hydrofluoric acid, now that these reagents are so readily obtainable in sufficient purity, the latter in ceresine bottles.

The numberings of the paragraphs are unchanged, and, generally, these are thrown into an improved form, all additions being brought in under sub-heads. Many valuable additions to the methods of determination have been introduced, among which are: Penfield's estimation of fluorine, Rose's estimation of carbon dioxide by volume, the precipitation of zinc sulphide in a hot solution, the precipitation of manganese by bromine and ammonia, the decomposition of silicates by sulphuric and hydrofluoric acids, Schulze's estimation of nitric acid, and a full and clear description of basic acetate precipitation. A satisfactory description of Dr. J. Lawrence Smith's method of estimating alkalies in silicates is given, but, unfortunately, this latter operation is twice indexed as a method of determining silica.

Dr. Gibbs' method of precipitating copper oxide by sodium carbonate is given, but there is no mention of the addition of sodium hydroxide, which addition affords a very satisfactory modification of this otherwise troublesome process (see Proc. Am. Chem. Soc., II., No. 4).

The precipitation of alumina by ammonia is properly improved by shortening the time of heating, but the use of paper pulp to promote the washing of this precipitate is not mentioned.

Some excellent methods of procedure now in use by analysts, which one might have expected to find here, have been omitted, especially the ignition of some sulphides under hydrogen sulphide, which is to be preferred to hydrogen, in determining cuprous sulphide, lead sulphide, cobalt sulphide, zinc sulphide, etc. (Ztschr. anal. Chem., **19**, 172).

Quite a number of important modifications of older methods have been given in the appendix of Vol. II., which one would expect to find in Vol. I. or at least referred to there, such as the proper method of precipitating ammonium magnesium phosphate, the washing of "yellow precipitate" with diminishing amounts of ammonium nitrate in lieu of molybdate solution, Dr. Gooch's use of amyl alcohol to separate lithia, Weller's method of detecting and estimating titanic oxide by hydrogen dioxide.

In Volume II. we find also a number of new processes

given in detail, including the following: The use of Johnson and Jenkins' azotometer, the methods of Clennell and of Handy for zinc, Gautier's separation of arsenic according to Johnson and Chittenden, electrolytic separation of lead by Hollard and of copper by Gooch, Oma Carr's estimation of tannic acid, G. Tate's method for silica in ferro-chrome, and a volumetric estimation of manganese by F. W. Daw. Dr. Gibbs' use of a comparison tube in measuring gases is described, also an improved form of purifier for oxygen is mentioned, which suggests the omission of the very efficient and compact apparatus devised for this purpose by F. G. Benedict (see this JOURNAL, **23**, 332). There is also given an improved method of burning carbon from iron in oxygen, but no notice has been taken of the excellent suggestion of T. W. Hogg of the use of a mixture of ferric and cupric chlorides for the separation of carbon from iron or steel (see Chem. News, **58**, 199).

When a full table of the strength of acetic acid by Oudemans was given on page 291, there does not appear any reason for the translator adding, on page 318, a similar table by Mohr, which has less range and is not definite as to temperature.

In the examples for practice, a peculiarly full and lucid description is given of the exact process in the determination of chlorine in sodium chloride, which will prove of much value as a lesson in accurate manipulation to any beginner in analysis.

In Appendix I. we find in full the official methods of analysis of the agricultural chemists, being a reprint of Chemistry Bulletin No. 46 of the U. S. Department of Agriculture, so presenting in a convenient and permanent form data which every analytical chemist should have at hand.

In Appendix II. we have a reprint of the admirable paper on mineral analysis by Dr. W. F. Hillebrand, as published in Bulletin No. 176 of the U. S. Geological Survey. This includes quite a number of the more recent improved methods, to which, as before noted, it would have been well to have referred in the schemes given in Volume I.

The very full index is presented in a clear and attractive form and the work of the printer is well done throughout the book. F. P. D.

THE PHASE RULE AND ITS APPLICATIONS. By ALEX. FINDLAY, M.A., PH.D., D.SC., Lecturer and Demonstrator in Chemistry, University of Birmingham; with an INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY, by SIR WILLIAM RAMSAY, K.C.B., F.R.S. New York: Longmans, Green & Co. 1904. pp. 313.

Only words of praise can be spoken for this admirable little

book. We have at last a treatise on the Phase Rule in English, which is clear, concise, and intelligible to any earnest student of physical chemistry. This book compares favorably with the more elaborate treatise in German on the same subject by Roozeboom.

The most important chapters are on Typical Systems of One Component; Systems of Two Components—Dissociation; Solutions of Gases, Liquids, Solids; Systems of Three Components; Systems of Four Components.

The work is prefaced by an introduction to Physical Chemistry by Sir William Ramsay, which is really a brief, historical sketch of physical chemistry from the earliest time. The work can be heartily recommended to every one who wishes to become familiar with the development of this important generalization, which we owe originally to our distinguished countryman, Willard Gibbs, but which has been developed in the hands of modern physical chemists. H. C. J.

A LABORATORY MANUAL OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY FOR STUDENTS IN MEDICINE. By DR. E. SALKOWSKI, Professor in the University and Director of the Chemical Laboratory of the Pathological Institute, Berlin. Authorized translation from the second revised and enlarged German edition. By W. R. ORNDORFF, A.B., PH.D., Professor of Organic and Physiological Chemistry in Cornell University. First edition. New York: John Wiley & Sons. pp. 263.

The translation of Salkowski's Practicum will be welcomed by all physiological chemists who have to do with the teaching of the subject on account of the number of medical students who cannot read German satisfactorily. Ever since this work was written it has been the model of laboratory manuals in physiological chemistry. In some respects the work has not been kept up to date, however. On page 49 the decomposition of hydrogen peroxide by blood is spoken of as the "so-called catalytic action of the blood pigment." It was shown by Bergengruen, in 1888, that pure hemoglobin does not decompose hydrogen peroxide, and that the action of blood on hydrogen peroxide is due to the stroma of the red blood corpuscles. Again, the work of Schiff on the biuret reaction might have been mentioned, and also the work of Hopkins and Cole on tryptophan.

Again, Salkowski's old method for the separation of the xanthine bases is given instead of the far more satisfactory method of Krüger and Salomon, which is now almost exclusively used.

The translation is clear and satisfactory and it deserves to be largely used. A. S. L.

CONTENTS.

PAGE.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE:

On Certain Sulphamido Derivatives of Furfurane. By H. B. Hill and J. P. Sylvester 185

On the Action of Potassic Nitrite on Mucobromic Ester By H. B. Hill and O. F. Black 228

A METHOD FOR THE DETERMINATION OF CHLORIC ACID. By W. S. Hendrixson 242

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY:

On the Solubility of Barium and Mercuric Chlorides. By H. W. Foote and H. S. Bristol 246

On the Solubility of Potassium and Barium Nitrates and Chlorides. By H. W. Foote 251

ON SOME CUPRAMMONIUM SULPHATES. By David W. Horn and Edytha E. Taylor 253

THE DECOMPOSITION OF NITROSO COMPOUNDS. By William A. Noyes and René de M. Taveau 285

REVIEWS.

Die Kathodenstrahlen 293

Immune Sera: Hæmolysins, Cytotoxins, and Precipitins . . 294

Laboratory Exercises in Physical Chemistry 296

Entered at the Post-Office at Baltimore, Md., as second-class matter, December 10, 1891.

American Chemical Journal.

This Journal contains original articles by American chemists; reviews of works relating to chemistry; reports on progress in the various departments of chemistry; and items of general interest to chemists. Twelve numbers of about 100 pages each are published annually, at regular intervals, and form two volumes. A number is issued each month. The subscription price is $5.00 a year in advance; single numbers 50 cents.

Fifty copies of each original communication will be furnished, if requested, without charge; any larger number can be obtained at a slight additional expense to the author.

Communications concerning subscriptions should be addressed to The Johns Hopkins Press, Baltimore, Md. Editorial communications should be addressed to the Editor, IRA REMSEN, Baltimore, Md.

PRINTED BY THE CHEMICAL PUBLISHING COMPANY,
EASTON, PA.

C. O. Baker, Pres. C. W. Baker, Vice-Pres.

Baker & Company, Inc.

ARTISANS IN PLATINUM

408-410-412-414 N. J. R. R. Ave.

Newark, N. J.

Platinum

In Any Form

For Any Purpose

Platinum ware of the standard shapes and sizes always carried in stock.

Our data concerning **Platinum** sent free upon request.

Sole licensees for the manufacture of the Shimer Crucible.

NEW YORK OFFICE, 120 LIBERTY ST.